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REPORT ON FINE GRID SAMPLING PLAN (FOR TCDD AND 2, 3, 7, 8-TCDD) Volume Two

Hercules Incorporated
Wilmington, Delaware

IT Corporation
Knoxville, Tennessee

RESPONSIVE TO THE NEEDS OF ENVIRONMENTAL MANAGEMENT

REPORT ON FINE GRID SAMPLING PLAN

(FOR TCDD AND 2,3,7,8-TCDD)

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VOLUME TWO: ATTACHMENTS

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ATTACHMENT 1

A SAMPLING STRATEGY FOR CLEAN-UP OF DIOXIN IN SOIL

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Submitted to:

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1.0 SUMMARY

The soil at a number of sites in the state of Missouri has been contaminated with dioxin. Soil sampling conducted at these sites has resulted in the demarcation of areas that are scheduled to be cleaned by excavating soil. After the top layer of soil is removed, the question arises as to whether additional cleanup with depth or in adjacent areas is required. The primary purpose of this paper is to describe a sampling design (strategy) for answering this question.

There are many factors that must be considered in developing such a sampling strategy. These include analytical capability and cost for measuring dioxin, budget constraints, various statistical concerns (discussed below), as well as risk assessments of human exposure, prediction of dioxin's impact on the environment, and legal issues such as whether a site that undergoes cleanup remains a hazardous material site. Social concerns must also be addressed. The emphasis in this paper is on statistical issues.

An outline of the proposed sampling strategy for making soil removal decisions is as follows:

1. Divide the known contaminated land area into units ("clean-up units") of a size conducive to the use of appropriate soil removal apparatus (e.g., large earth moving equipment). We assume here that the clean-up unit is 20 by 250 feet, a practical size for the Missouri sites since dioxin contamination is frequently along roadways and large earth-moving equipment will be used in the clean-up operation.

2. Adjacent to the area where cleanup is to be initially conducted, establish a ring of additional clean-up units. These "adjacent" units will be sampled in the same way as the other units to check for lateral spread of dioxin on surface soil.

3. Remove surface soil in those units scheduled for clean up on the basis of prior data.

4. In each unit where soil is removed, and in all adjacent units established in step (2) above, set up two sampling lines parallel to the long axis of the unit, 10 feet apart and 5 feet from each side of the unit. Place markers every 10 feet along these lines starting 5 feet from one end.

5. Form a total of 3 or more (n) composite samples by collecting and pooling 50 small soil samples from the unit into each composite. Details of this sampling and compositing procedure are given in the body of this report.

6. Randomly select m aliquots of soil from each of the composites and analyze each for dioxin. This gives mn = N data for each clean-up unit.

7. Use the N data to estimate the arithmetic mean, $\bar{x}$, and the standard deviation, s, of the n composite means. Then use $\bar{x}$ and s to compute an upper confidence limit on the true mean concentration for the clean-up unit. If this upper limit exceeds the decision criterion D (an acceptable true mean concentration [ppb] of dioxin in the top 2 inches of soil over the entire unit), then a layer of soil is removed from the unit using earth moving equipment. Otherwise, no soil is removed.

8. If soil is removed from an adjacent unit, then an additional adjacent unit adjacent to the first is established and the above sampling plan and decision rule applied to it. The rationale for the above approach and some complications that may arise in practice are discussed in this paper.

An important potential limiting factor in the use of any sampling strategy is the cost and turnaround time associated with the analytical method used to analyze soil for dioxin. The currently accepted analytical method (the CLP method) can be used at the clean-up site at a rate of 20 to 25 samples per 24-hour period by using a mobile laboratory. Alternatively, a fixed laboratory in St. Louis, Missouri, can do a similar sample load.

2.0 RECOMMENDATIONS

Based on the discussion in this report, the following recommendations are made concerning the implementation of a soil sampling strategy at dioxin contaminated sites in Missouri:

1. Consideration should be given to basing soil removal decisions on an acceptable (allowable) true average concentration D (the decision criterion).

2. Demonstrate a procedure for compositing and adequately mixing dioxin soils from Missouri. The sampling strategy discussed here assumes the mixing process thoroughly homogenizes the soil so that the mixture has a uniform concentration of dioxin, even though individual samples entering the composite may have different concentrations.

3. Evaluate the sampling strategy discussed in this paper by applying the method to a clean-up unit. Collect five or more composite samples from the unit in the suggested manner and analyze three or more aliquots from each to quantitate the variability in dioxin concentrations between and within composites. This information can then be used to approximate, for the soil removal operation, the number of composites and the number of aliquots per composite

3.0 INTRODUCTION

In January 1984, U.S. EPA decided to clean up six dioxin-contaminated sites in Missouri. This decision projected the excavation of contaminated soil, transport to Times Beach, and storage in a specially designed depository. Costs for these carefully designed cleanup efforts are large, about $300/cu.yd. Therefore, it is important to clean up areas in a rational manner which takes into account excavation and analysis costs and many social concerns. Some of the contaminated sites were proposed for immediate removal actions. IT Corporation (IT), under subcontract to Environmental Emergency Services Company (EES), the ERCS contractor for Zone 4, was requested to address some pressing needs for developing appropriate excavation plans.

Considerable data exist on the extent of contamination at the various sites, and the proposed areas requiring excavation can be identified with reasonable certainty. However, two major uncertainties remain. The first unknown, which is the subject of this paper, is the definition of a clean area at the border of presently contaminated sections and the definition of a clean area after initial excavation activities. The second uncertainty is the distribution of dioxin with depth. A recent study [1] confirms that existing dioxin data as a function of depth are suspect because of potential contamination during sampling activities.

Four of the six areas proposed for cleanup during 1984 remain inhabited. A renewed sampling effort to define the areal and vertical contamination more rigorously than currently available was deemed socially unacceptable.

A constraint on any soil removal operation is that current analytical procedures for dioxin in soil [2] are time-consuming and expensive. If excavation/restoration activities are delayed because of analytical restrictions, the cost of idle equipment and manpower can also be large. Further, it is desirable to minimize the time that an excavated area remains exposed to erosion by wind or rain.

This paper focuses on a scientifically defensible sampling strategy that is achievable within currently anticipated socially and economic conditions.

4.0 IMPORTANT CLEAN-UP CONSIDERATIONS

Cleanup of a contaminated area requires definitions of: (1) what is being measured; (2) what criterion is used to make clean-up decisions; (3) various statistical quantities that define a decision rule for when to remove soil; (4) a field sampling plan for obtaining representative dioxin concentration data; and (5) action guides.

Concerning item 1, in the present case 2,3,7,8-tetrachlordibenzo-p-dioxin is the major toxicant of concern. However, since this dioxin isomer is 98 to 100% of the total dioxin concentration at Missouri sites [3], the clean-up criterion can be set equally well for total tetrachlorinated dibenzo dioxins. The use of this definition can result in a slightly faster analysis than for the specific isomer.

Item 2 requires definition of a clean-up unit (area) and an acceptable average dioxin concentration (decision criterion). Selection of a clean-up unit size depends on site characteristics, exposure estimates, and practical concerns. The sampling strategy developed below defines the decision criterion, D, to be that true mean concentration in the top 2 inches of soil in the entire cleanup unit that does not require the removal of soil. Selection of a specific value for D is beyond the scope of this paper, but such a selection must be based on a risk assessment of human and environmental exposure, as well as on legal, social and political factors. For illustration purposes we use D = 1 ppb in this paper. We also assume the clean-up unit is 20 by 250 feet in size.

Item 3 concerns the definition of a decision rule that makes use of D and data from the cleanup unit in question to decide whether soil removal is needed. The rule suggested here is to compute an upper confidence limit on the true concentration for the unit and to remove soil if that limit exceeds D. The computation of the confidence limit requires the specification of Ca, the prespecified small risk (probability) of not removing soil when in fact the true average concentration for the unit exceeds D. We must also assume that the composite sample means are normally (Gaussian) distributed. The details of this suggested procedure are given in Section 5.4.

Item 4 concerns the definition of the number and location of soil samples removed from the unit (discussed in Sections 5.5 and 5.6), whether compositing of samples is done, and the number of dioxin analyses conducted. To reduce analytical costs and satisfy the assumption of normally distributed composite means mentioned above, the use of composite sampling is suggested. However, it must be understood that the compositing approach is not ideal if the primary goal is to find small hot spots since compositing dilutes (averages out) hot spots. Furthermore, compositing requires a procedure for thoroughly mixing and homogenizing individual soil samples. If the mixed composite sample is inhomogeneous, then the standard deviation of

the composite means, s, (see equation 1 in section 5.4) will be too large and the decision to remove soil will be made more frequently. Hence, to avoid unnecessary removal of soil, a good mixing procedure is needed.

Item 5 (action guides) refers to developing clear responses to the following questions:

- If the decision rule indicates soil removal is required, must the top layer of soil over the entire clean-up unit be removed?
- If points of contamination (hot spots) are found, must the whole top layer of soil or just the hot spot be removed?

The answer to the first question would appear to be "yes" if the sampling strategy described below is used, i.e., if composites are formed by mixing small soil samples collected from all parts of the unit. Concerning the second question, if a hot spot is found and only that spot removed, individual or composite samples must be collected to provide assurance that the remainder of the unit meets the decision criterion. In practice it may be simpler to always remove the top layer of soil from the entire unit unless the unit is very large, generating large amounts of soil to transport and store. Probabilities of missing hot spots can be evaluated using methods given in [8] and [9].

5.0 A SAMPLING STRATEGY

5.1 Main Features

The sampling strategy developed here has the following main features:

1. Soil removal decisions are made for entire clean-up units.

2. Soil removal with depth occurs in stages.

3. Each stage involves collecting composite samples from the exposed soil surface. Randomly chosen aliquots from each composite are analysed for dioxin.

4. Soil removal decisions are made individually for each clean-up unit by comparing a computed upper confidence limit against the decision criterion D.

5. Soil removal laterally occurs sequentially by sampling and applying the decision criterion to cleanup units adjacent to units where soil removal has occurred.

The chances of missing hot spots when removal decisions are based on composite samples is discussed in Section 5.8.

5.2 Establishing Clean-Up Units

The assumption is made here that prior sampling for dioxin has identified areas where soil removal is clearly required. Surface soil to a depth deemed appropriate on the basis of past data will be removed for these areas. This soil will be either temporarily stored at the site or loaded immediately on trucks for transport to a suitable disposal area. The area where soil removal has occurred is then divided into clean-up units. Decisions concerning future soil removal are made for individual clean-up units so that any additional soil removal proceeds unit by unit.

Next to each outermost unit in the area where soil has been initially removed, (which includes areas where the original soil surface has been substantially disturbed or where soil from the soil removal operation may have been inadvertently deposited) an adjacent unit is established as illustrated in Figure 1. These adjacent units are subjected to the same sampling and compositing scheme and the same decision criterion and decision rule as the original units. Figure 1 shows four cleanup units, U415, U425, U435, and U445 along a road where initial soil removal has occurred. Also shown are adjacent units that will be sampled and evaluated for possible soil removal. If soil removal is necessary in any adjacent unit, then another unit adjacent to it is established and the same sampling strategy and decision criterion is applied.

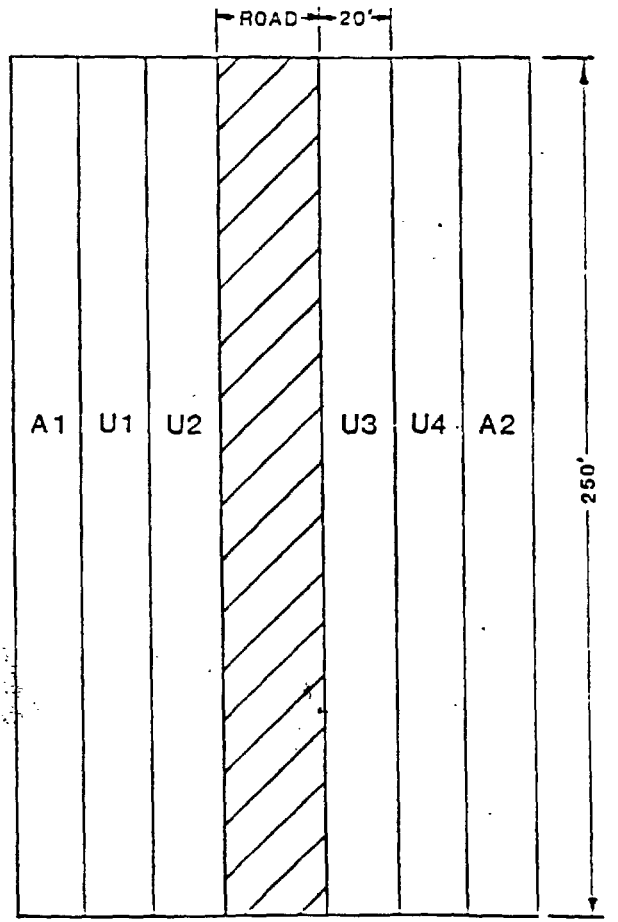


ILLUSTRATION of EXCAVATION UNITS U1,U2,U3,U4
and ADJACENT TEST UNITS A1 and A2
for CLEANUP of CONTAMINATED ROAD

FIGURE 1

For each clean-up unit soil removal occurs in stages with depth. Soil samples are collected from the top 2 inches of exposed soil and an additional layer of soil removed if use of the decision criterion so indicates. In practice it may not be practical to establish and sample adjacent units until all layers of soil have been removed from the original clean-up area.

Using the above approach, soil removal with depth and horizontally is continued until no soil removal is required in any unit at any depth. Note that this sequential approach assumes that an absence of dioxin at one depth implies an absence of dioxin at greater depths. This assumption may be reasonable based on a knowledge of how dioxin was originally applied and its movement through soil, or on information from the samples initially taken to define the original soil removal area. If reasonable doubt remains, then some proportion of the cleanup units should be sampled at depth using trenching techniques as a double check.

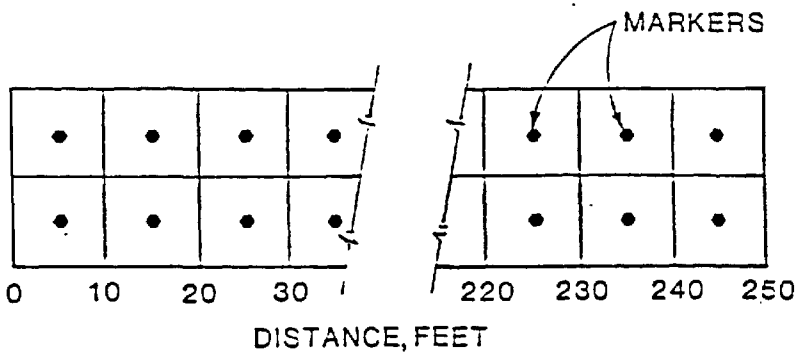
In a few locations, it will not be reasonable to exactly follow the sampling protocol specified above because of such problems as steep terrain, obstruction, etc. With adequate planning, these situations can be identified in advance of the field operations and an alternative and equivalent clean-up area may be chosen through consultation between the scientific and field personnel. Any such alterations must be thoroughly documented in order to not invalidate the data analysis.

5.3 Sampling and Compositing

As indicated above, we assume that each cleanup unit is 20 by 250 feet in size. If other sizes are used, the general sampling and compositing approach described here can be easily adapted.

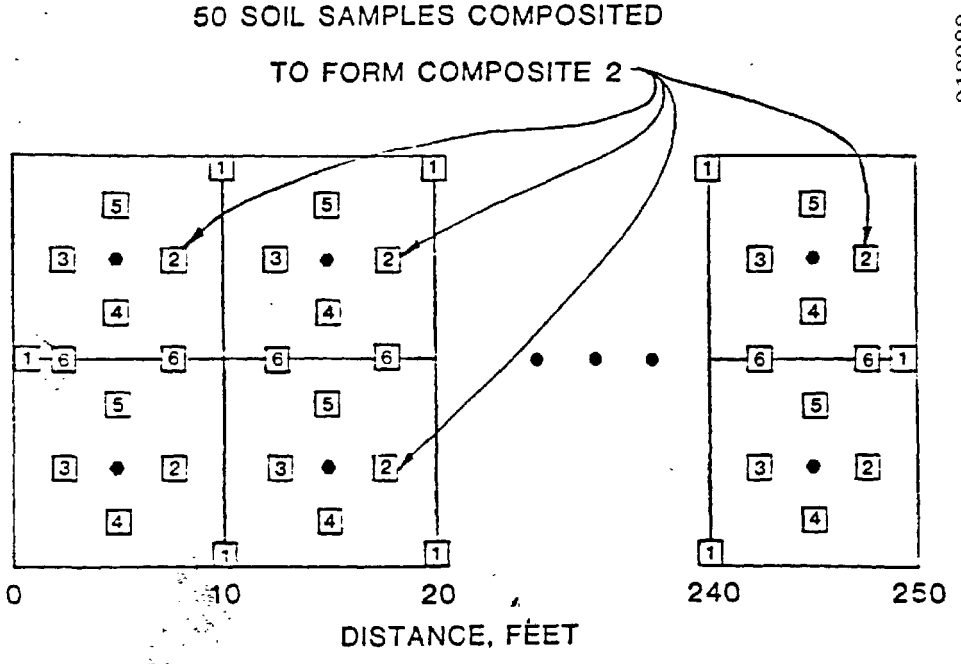
Each clean-up unit is divided into 50 equal blocks of size 10 by 10 feet by setting up two lines parallel to the long axis of the unit, 10 feet apart and 5 feet from each side of the unit. Markers are then placed every 10 feet along these lines starting 5 feet from one end. Each marker is at the center of a 10 by 10 foot block as illustrated in Figure 2.

A minimum of three composite samples should be obtained from each clean-up unit according to the systematic pattern shown in Figure 3. Referring to Figure 3, composite number 1 consists of 50 soil samples pooled together, where a single sample is collected within each of the 50 one-square foot areas labeled with the number 1 that lie around the periphery of the clean-up unit. Similarly, composite number 2 consists of 50 samples pooled together, where each sample is taken 3 feet north of a stake, and so on for the remaining composites. The "sample" within each one-square foot area consists of four spoonfuls of soil of approximately equal weight taken from the top 2 inches of soil. Hence, a composite sample consists of 200 spoonfuls of soil collected in a container that will allow homogenization by ball-milling, blending, or some other mechanical procedure. The use of spoons for obtaining



A 20ft by 250ft CLEANUP UNIT DIVIDED INTO 50 EQUAL SIZED BLOCKS

FIGURE 2



SYSTEMATIC SAMPLING DESIGN FOR FORMING THE FIRST 6 COMPOSITE SAMPLES

FIGURE 3

each "sample" will allow for rapid collection of the 50 samples needed for each composite. However, a preferred method is to use a small soil corer of constant size and depth at each of the 50 locations. This would provide a consistent soil volume and depth.

If four, five, or six composites are collected, they should be taken at the locations indicated in Figure 3 (i.e., we note from Figure 3 that the sixth composite will consist of only 48 samples rather than 50 as for the other composites). If more than six composite samples are required (see section 5.5), each additional composite should be obtained by choosing at random a location within a 10 by 10 foot block and collecting a sample (four spoonfuls) at the same position in all 50 blocks, and pooling the samples.

Following thorough mixing and homogenization of each composite, one or more (m) aliquots from each composite are chosen at random and analyzed for dioxin. If n composites are collected, then a total of nm data are available for computing the upper confidence limit for making the soil removal decision as described below.

The sampling and compositing plan given above has two important advantages over analyzing single grab samples for dioxin. First, by pooling many small samples across the entire unit each dioxin datum is an estimate of the average for the entire unit, not just for a small local area. This is important since the decision criterion D is defined to be the acceptable average concentration for the entire unit. Second, the compositing process is a mechanical way of averaging out variabilities in concentrations from place to place over the unit. Hence, the resulting dioxin concentrations should tend to be more normally (Gaussian) distributed than individual grab samples. This is important since normality is required when computing the upper confidence limit. However, these two advantages will be lost unless the 50 samples going into each composite are thoroughly mixed and homogenized. Also, compositing tends to mask local hot spots as discussed in Section 5.8.

5.4 Making Clean-up Decisions

The decision whether to remove the surface soil that has been sampled in a particular unit is made using the following decision rule: remove soil if and only if

$$\bar{x} + t_{\alpha, n-1}\, s/\sqrt{n} > D \qquad (1)$$

where $\bar{x} + t_{\alpha, n-1}\, s/\sqrt{n}$ is the estimated upper 100 $(1 - \alpha)$% confidence limit on the true mean for the unit, and D is the preset decision criterion discussed above. (α is defined below.)

This decision rule is a one tailed test of the null hypothesis

$$H_0 : \text{True dioxin mean} \geq D$$

versus the alternative hypothesis

$$H_A : \text{True dioxin mean} < D.$$

We reject H_0 and hence do not remove soil if Equation 1 is satisfied, i.e., if $\bar{x} + t_{\alpha,n-1}\, s/\sqrt{n} < D$.

Clearly, to use this decision rule we must compute $\bar{x}$ and s, where

$$\bar{x} = (mn)^{-1} \sum_{i=1}^{n} \sum_{j=1}^{m} x_{ij}$$

= arithmetic mean of the nm dioxin concentrations x_{ij},

$$s = \left[(n-1)^{-1} \sum_{i=1}^{n} (\bar{x}_i - \bar{x})^2 \right]^{1/2}$$

= standard deviation of the n composite means $\bar{x}_i$,

$$\bar{x}_i = m^{-1} \sum_{j=1}^{m} x_{ij}$$

= arithmetic mean of the m aliquot concentrations from the ith composite.

We also need $t_{\alpha,n-1}$, which is the value that cuts off $100\,\alpha$ % of the upper tail of the t distribution with n-1 degrees of freedom. α is the prespecified small risk (probability) of not cleaning a dirty area, when in fact the true mean for the unit (in top 2 inches of soil) equals or exceeds D. Hence, the decision procedure is to choose a value for D and for α (e.g., $\alpha = 0.01$ or 0.05), find $t_{\alpha,n-1}$ the t tables and see whether the upper confidence equals or exceeds D. If it does, then the rule requires the removal of soil. If not, the rule requires no removal of soil.

The tabled value $t_{\alpha,n-1}$anges depending on n for a given α. For example, if $\alpha = 0.05$, then $t_{0.0,n-1}$ varies from 2.92 for n = 3 to 2.01 for n = 6, to 1.80 for n = 12. If we set $\alpha = 0.01$, then $t_{0.01,n-1}$ 5varies from 6.96 to 3.36 to 2.72 for n = 3, 6, and 12, respectively. The t tables from which values of $t_{\alpha,n-1}$ are obtained are found in most statistics books, e.g., [10].

Note that if equation (1) is solved for $\bar{x}$, we obtain

$$\bar{x} > D - t_{\alpha,n1-1}\, s/\sqrt{n}. \qquad (2)$$

Hence, for specified values of D, α, s and n, equation (2) gives the value of x below which the decision rule in equation (1) indicates that no soil removal is required.

Rather than specify s, we may choose to specify the relative standard deviation of the composite means, $C = s/\bar{x}$, in which case we replace s in equation (1) with Cx. (In general we expect C to be more constant than s from one cleanup unit to the next. Hence, C is usually preferred for planning purposes.) Suppose for illustration that D = 1 ppb. Then solving equation (1) for x gives

$$\bar{x} > 1/[1 + t_{\alpha,n-1}\, C/\sqrt{n}]. \qquad (3)$$

Table 1 gives values of x obtained using equation (3) for selected values of C and n for α = 0.05, 0.01 and D = 1. For example, if α = 0.01, n =3 and $C = s/\bar{x} = 0.25$, then soil must be removed if $\bar{x} > 0.50$ ppb. But if the standard deviation s is larger so that, e.g., C = 0.50, then soil removal is required if $x > 0.33$ ppb.

5.5 Choosing the Number of Composites

In Section 5.3 we suggested that a minimum of 3 composite samples be obtained from each unit and the first (up to 5) composites be collected according to the pattern in Figure 3. If 5 composites are taken, this pattern gives good coverage of the entire unit.

In this section we give a method [using equation (4) below] for choosing n that is based on controlling the chances of making cleanup decision errors to acceptably low levels. This approach may indicate an n greater than 5. In that case we suggest each additional composite sample also be composed of 50 small samples collected over the 50 blocks as explained above.. The relative location where each small sample is taken for a given composite should be the same in each block, that location being chosen at random. If the approach for n given below should result in an n less than 5, we suggest the composite samples be chosen in the order of their number in Figure 3. For example, if n = 4, then composites numbered 1, 2, 3 and 4 in Figure 3 are collected. However, if fewer than 5 composites are taken, the advantage of good coverage of the entire unit is not realized. This may be reason to require $n > 5$.

The method for determining n given below requires an estimate of the variance σ^2, of all possible composite means that could conceivably be obtained from the unit. In practice, σ^2 is estimated by collecting several composites in a preliminary study in one or more clean-up units. Also, as

clean-up units are sampled during the cleanup process, the estimate of σ^2 can be updated using the additional data. We will see below that if σ^2 large, more composites are required.

TABLE 1

Observed Average Dioxin Concentrations x (ppb) Below which no Soil Removal is Required when the Decision Criterion D is 1 ppb and when the Relative Standard Deviation of the Composite Means, C, Equals 0.50, 0.25 or 0.10

	C[1] = 0.50		0.25		0.10	
Number of Composites n	α^2 = 0.01	0.05	0.01	0.05	0.01	0.05
2	0.08	0.31	0.15	0.47	0.31	0.69
3	0.33	0.49	0.50	0.66	0.71	0.86
4	0.47	0.63	0.64	0.77	0.81	0.89
5	0.54	0.68	0.70	0.81	0.86	0.91
6	0.59	0.71	0.74	0.83	0.88	0.92
12	0.72	0.79	0.84	0.89	0.93	0.95
30	0.82	0.87	0.90	0.93	0.96	0.97

[1] C = Relative standard deviation of composite means = s/x.

[2] α = Prespecified probablility we are willing to take of not removing soil when in fact the true mean for the unit equals or exceeds D.

The choice of n using the method given below also depends implicitly on budget constraints, turnaround time of the dioxin analytical procedure and other practical constraints. It also depends explicitly on the value of D relative to a smaller mean value μ^0 , , (explained below), and on the risks (probabilities) we are willing to assume of making the two types of clean-up decision errors. These errors are called Type I and Type II errors and are defined as follows:

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Type I: Error of not removing soil when the true mean n equals or exceeds D, i.e., of not cleaning a dirty area.

Type II: Error of removing soil when the true mean concentration equals μ^0 , where $\mu^0 < D$, i.e., of cleaning a clean area.

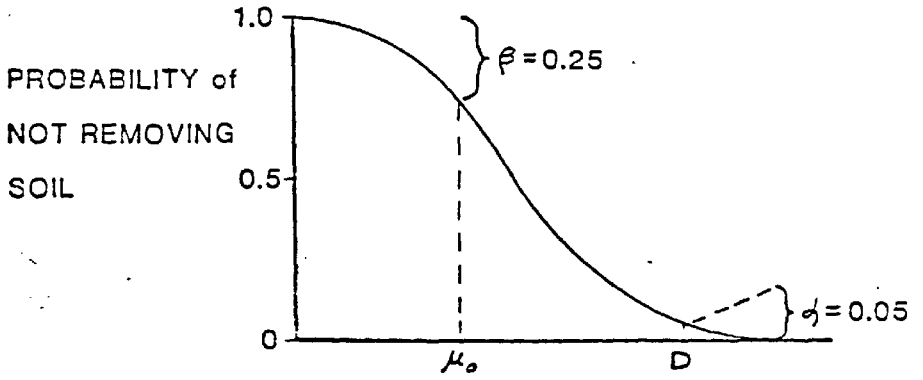
The probability of a Type I error is denoted by α , the same quantity used in equations 1, 2, and 3 above. The probability of a Type II error is denoted by β . Ideally, we would like both α and β to be very near zero, but this may require collecting many composites. In practice there is a trade off between what the budget and other practical concerns will allow, and the complete assurance ($\alpha = \beta = 0$) we would ideally like to achieve that no decision errors are made.

The method suggested for choosing n or for evaluating the costs and benefits of choosing various values for α , β , D and μ^0 is to compute (see [7], pp. 325-328 for derivation)

$$n = (Z_\alpha + Z_\beta)^2 \left[\sigma / (D - \mu^0)\right]^2 \qquad (4)$$

where D is the chosen decision criterion, Z_α is the value that cuts off $100\ \alpha$ % of the upper tail of a standard normal (Gaussian) distribution (with a like definition for Z_β), σ is the standard deviation of all possible composite means that could conceivable be obtained from the clean-up unit, and μ^0 is a mean concentration less than D, such that, if actually present, the probability of removing soil from the unit is β . Values of Z_α and Z_β are tabled in most statistics books, e.g. [10]. Values of Z_α for $\alpha = 0.05$ and 0.01 are 1.654 and 2.33, respectively.

Equation (4) gives the number of composites that must be collected to assure that the probability is not greater than α of failing to remove soil when $\mu > D$, and the probability is no greater than β of incorrectly removing soil when $\mu\mu > \mu^0$. The relationship between the chosen values of α, β, D and μ^0 is shown in Figure 4. In practice, β might be chosen to be larger than α since it is more important to limit undue exposure to higher than allowed mean levels of dioxin than to prevent unnecessary removal of soil. The validity of equation (4) depends on the composite means being normally distributed and on an advance estimate of σ for the unit. An advance estimate of Cs may be obtained by conducting preliminary sampling studies as indicated above. The normality assumption may not be unreasonable



PROBABILITY of NOT REMOVING A LAYER of SOIL FROM THE CLEANUP UNIT FOR A RANGE of POSSIBLE VALUES of THE TRUE MEAN DIOXIN CONCENTRATION

FIGURE 4

since each composite sample is the sum of 50 smaller soil samples. Hence, assuming the mixing process thoroughly homogenizes and mixes the small samples, the Central Limit Theorem (see, e.g., [5]) should apply. This theorem states that the average of several data values is closer to normality than the data values themselves. In the case of composite samples, the mixing process is a mechanical way of averaging the 50 small samples. The normality assumption should be evaluated statistically on the basis of preliminary data and data obtained during the clean-up operation.

Table 2 gives values of n computed using equation (4) for the case where D = 1 ppb and for various choices of α, β, μ_0 and σ. Table 3 gives values of $(Z_\alpha + Z_\beta)^2$ that may be used in equation (2). Our understanding of Figure 4 and the results in Table 2 may be aided by considering μ_0 and D as defining "good" and "bad" units in the sense we have a strong preference for not removing soil when the true mean concentration is less than μ_0, and we have a strong preference for removing soil when the true mean equals or exceeds D. If the true mean is greater than D or between zero and μ_0, we are willing to tolerate only small probabilities of making wrong decisions. If the true mean is between μ_0 and D, we are less concerned whether or not soil is removed. Once the pairs (α, D) and (β, μ_0) are chosen, and if a good estimate of σ is available, equation (4) gives the number of composites needed to achieve this specification.

Table 2. The Number of Composites, n, obtained using Equation (4) when D = 1 ppb

α	β	μ^0	σ = 0.20	σ = 0.40	σ = 0.60
0.01	0.25	0.20	3	5	8
		0.50	4	8	15
		0.70	6	18	38
		0.80	8	38	83
		0.85	18	66	146
0.01	0.45	0.20	3	4	6
		0.50	3	6	11
		0.70	5	13	26
		0.80	8	26	57
		0.85	13	45	99
0.05	0.25	0.20	3	4	6
		0.50	3	6	10
		0.70	5	12	24
		0.80	8	24	51
		0.85	12	41	89
0.05	0.45	0.20	3	3	4
		0.50	3	4	7
		0.70	4	8	15
		0.80	6	15	31
		0.85	8	25	53

Table 3. Values of $(Z_\alpha + Z_\beta)^2$ for Use in Equation 4 to Estimate N when the Normality Assumption is Tenable. α and β are Probabilities of not Cleaning a Dirty Area and of Cleaning a Clean Area, Respectively

β/α	.0001	.001	.01	.05	.10	.15	.20	.25	.30	.35	.40	.45
.0001	55.32	46.37	36.55	28.77	25.01	22.61	20.80	19.30	18.01	16.85	15.78	14.78
.001	46.37	38.20	29.34	22.42	19.11	1703	15.46	14.17	13.07	12.08	11.18	10.
.01	36.55	29.34	21.65	15.77	12.02	11.31	10.04	9.005	8.13	7.353	6.654	6.012
.05	28.77	22.42	15.77	10.82	8.564	7.189	6.183	5.380	4.706	4.122	3.603	3.135
.10	25.01	19.11	13.02	8.564	6.570	5.373	4.508	3.826	3.262	2.779	2.356	1.980
.15	22.61	17.03	11.31	7.189	5.373	4.296	3.527	2.927	2.436	2.021	1.633	1.350
.20	20.80	15.45	10.04	6.183	4.508	3.527	2.833	2.299	1.866	1.505	1.119	0.936
.25	19.30	14.17	9.005	5.380	3.826	2.927	2.299	1.820	1.437	1.123	0.861	0.640
.30	18.01	13.07	8.13	4.706	3.262	2.436	1.866	1.437	1.100	0.828	0.605	0.423
.35	16.85	12.08	7.353	4.122	2.779	2.021	1.505	1.100	0.828	0.5938	0.408	0.
.40	15.78	11.18	6.654	3.603	2.356	1.663	1.119	0.861	0.605	0.408	0.2566	0.144
.45	14.78	10.34	6.012	3.135	1.980	1.350	0.936	0.640	0.423	0.261	0.144	0.0632
.50	13.83	9.55	5.410	2.706	1.643	1.074	0.708	0.455	0.275	0.148	0.064	0.0158

A potential problem with the use of equation (4) is that the value of σ is likely to depend on the true mean concentration level, μ, present in the unit. For example, if $\mu = D$ a different value for σ should be used than if $\mu = \mu^0$. In practice, one could use an upper and then a lower limit for σ and see how n changes. Data obtained during the cleanup of initial units should help define the extent of this problem.

5.6 Choosing the Number of Aliquot Analyses per Composite

In the previous section we did not consider the question of how many aliquots, m, should be drawn at random from each composite for dioxin analysis. During preliminary sampling of clean-up units, m should be 5 or more from several composites. This will permit estimating the within composite variance by computing

$$s2_w = \frac{1}{n(m-1)} \sum_{i=1}^{n} \sum_{j=1}^{m} (\bar{x}ij - \bar{x}i)2 \qquad (5)$$

If $s2_w$ is large, then either there are large measurement errors in the dioxin analyses, and/or the mixing process has not achieved a truly homogeneous composite sample. The m aliquots per composite can serve as a quality control check on analytical variability over time, assuming the mixing process gives similar levels of homogeneity in all units.

A method for determining the optimum number of composites, n, and aliquots per composite, m, will now be given (see [10], pp. 531 for further discussion). This approach assumes the following cost function applies:

$$COST = c1n + c2nm \qquad (6)$$

where c1n is the cost associated with collecting and mixing n composite samples, c2nm is the cost of analyzing nm aliquots, their sum being the total dollars available for sample collection, mixing and analyses. We assume that c1 and c2 are known. The optimum value for m is estimated by computing

$$m = \left[\frac{c1/c2}{s2/s2_w} \right]^{-1/2} \qquad (7)$$

where $s2_w$ is obtained using equation (5) above, and

5.7 Concentration Near Measurement Detection Limits

All techniques discussed above assume there are no missing data due to the failure of laboratories to report dioxin concentrations that are below detection limits. Every effort should be made to insure that the best estimate of the actual concentration for each aliquot is reported to the data analyst. It is not acceptable to report zeros, the detection limit itself, or "less-than" numbers. Such reporting practices create difficult problems for the data analyst when computing $\bar{x}$ and s. However, all data reported for which the laboratory feels the aliquot contains less dioxin than can be measured with acceptable precision should be flagged so the data analyst will know these values are suspect.

5.8 Dealing with Hot Spots

Thus far in this report we have assumed that the average soil concentration (to some specified depth) over the entire clean-up unit (e.g., 20 by 250 feet) is the preferred criterion for deciding whether or not to remove additional soil from the unit. However, suppose the unit is "clean" except for one or more small hot spots. Then there is a finite probability that the individual samples collected over the unit (those that are composited) will not be taken at hot spot locations. In that case the unit will not be cleaned. But indeed even if the hot spot(s) is sufficiently large to have a high probability of being sampled, compositing 50 individual samples, only one or two of which have high concentrations, may result in the composite average being so low that the decision rule (equation 1) will still indicate cleanup is not required.

To illustrate this latter point, suppose six composite samples are formed, where each composite is obtained by pooling 50 individual samples collected over the clean-up unit as illustrated in Figure 3. Suppose 299 of the 300 individual samples contain no dioxin, but 1 sample has a concentration of 99.5 ppb. Then, 5 of the composite means will be zero and one composite mean will be 99.5/50 = 1.99 pbb (assuming perfect mixing of the 50 individual samples). Is cleanup required in this case? What does the use of equation 1 indicate? Suppose we choose $\alpha = 0.05$; then $t_{0.05,5} = 2.015$ (from the t tables). Also, the reader may verify that for this scenario, the value of s is calculated to be 0.812414. Therefore, equation 1 is

$$\bar{x} + t_{0.05,5}\, s/\sqrt{n} = \frac{99.5}{300} + 2.015\ (0.812414)/\sqrt{6} = 1 \text{ ppb}.$$

Hence, if D = 1 is used, the entire unit would be cleaned. However, if the one hot spot concentration had been less than 99.5 ppb, say 99.2 ppb, then $\bar{x} + t_{0.05,5}\, s/\sqrt{6}$ would be less than 1 ppb. Then the unit would not be cleaned and the hot spot would remain. For the above scenario,

$$s2 = (n-1)^{-1} \sum_{i=1}^{n} (\bar{x}_i - \bar{x})^2 \qquad (8)$$

is the estimated variance between composite means. Once m is obtained from equation (7), n may be obtained using the cost function [equation (6)].

As an example, suppose $s2/s2_w = 0.5$, i.e., the variability between composite means is half the variability between aliquots within composites. Further, suppose c1 = \$250 and c2 = \$450 so that c1/c2 = 250/450 = 0.556. Then equation 7 gives m = (0.556/0.5)1/2 = 1.05, which we round up to m = 2. Then if the total dollars available for each clean-up unit (20 by 250 feet) is, say \$5000, equation 6 gives 5000 = 250n + 450mn or n = 5000/(250 + 450m) = 4.3, which is rounded up to n = 5. Hence, if $s2/s2_w = 0.5$ is correct and the costs are as given above, we should analyse 2 aliquots from each of 5 composites.

It is important to get a good estimate of the ratio $s2/s2_w = 0.5$ for use in equation 7. This can be done by collecting data from the contaminated site using the same sampling design and compositing procedure to be used later during the clean-up phase. Some values of m and n for various values of $s2/s2_w$ are given below. These were obtained using equations 6 and 7 assuming COST = \$5000 and c1/C2 = 0.556.

$s2/s2_w$	m	n
0.05	4	3
0.10	3	4
0.50	2	5
0.60	1	8

This method of choosing n and m is appropriate when the goal is to estimate the true mean for the unit with maximum precision for fixed total cost. Maximizing the precision of $\bar{x}$ is clearly desirable since in that case the factor $s/\sqrt{n}$ (the estimated precision of $\bar{x}$) in equation (1) will tend to be smaller. This will result in fewer instances where soil is removed when the true mean is actually less than D. The optimum values of m and n would change from cleanup to cleanup unit if either s2 or $s2_w$ change (we assume costs will not change during the clean-up operation). Hence, in practice, if the same n and m are used in all units, the optimum cannot be uniformly achieved.

the concentration of the single hot spot could be as high as 99.4 ppb and equation 1 would still indicate no additional cleanup is required. Clearly, the possibility of leaving a hot spot (or several hot spots) is a disadvantage of the compositing method and the use of equation 1 as discussed in this report.

As another example, suppose one circular hot spot of size 100 square feet (diameter = 11.28 feet) and concentration 50 ppb is present within the clean-up unit. Suppose it is located so that one of the individual samples in each of the 6 composites hits the spot, e.g., the hot spot might cover the upper left 10 by 10 foot square in Figure 3. Then each composite mean will have a concentration of 50 ppb/50 samples = 1 ppb (assuming perfect mixing) and the average of the 6 composite means will also be 1. Since all composite means are identical, the standard deviation, s, of the composite means is zero. Then equation (1) givens $\overline{x} + 0 = 1$ ppb, which indicates cleanup is required if D has been set at 1 ppb.

Another scenario is where the contamination is uniform and slightly greater than 1 ppb over most of the cleanup unit, but a few local areas have zero concentrations. Hence, most of the unit should be cleaned if the true situation were known. However, if the zero concentration areas happen to be sampled, compositing may result in $\overline{x} + t_{\alpha=n-1}\, s/\sqrt{n}$ being less than D = 1. In that case no cleanup would be done.

There are many alternatives to the compositing design developed in this paper. For example, the size of the cleanup unit could be reduced and the number of composite samples increased. This would tend to reduce the dilution effect and increase the chances of cleaning units that contain hot spots. Or, the use of compositing could be abandoned and cleanup decisions made entirely on the basis of whether concentrations of individual (rather than composite) samples exceed D. However, if very small hot spots are important to find and remove, many individual samples would be required to have a high probability of finding them all. [These probabilities can be found using the techniques in (8) and (9)]. The dioxin analysis costs could be excessive in this case.

In practice there must be a balance between compositing and "looking for hot spots." People will differ in their assessments of what the optimum balance should be, especially since there is at present no definitive statistical guidance on optimum sampling strategies for cleanup situations. The approach in this paper puts more emphasis on compositing than on finding small hot spots. If the detection of hot spots is of overriding concern, then it becomes very important to define the size of hot spot that must be found and an acceptable risk of not finding it given that a specified grid spacing is used [discussed in (8) and (9)].

As an approximation to the methodolgy given in (8) and (9), we may state that in order to have a reasonable chance (greater than 90%) of finding hot spots the sampling grid must be approximately the same size as the diameter of the hot spots. Thus, for any practical sampling protocol it must be accepted that hot spots smaller than the design criteria will be missed.

Another attribute of hot spots that is often of concern is that very small hot spots that have extremely high concentrations should be more important than moderate size hot spots with moderate concentrations. Intuitively an 10 square foot area with a concentration of 500 ppb is more important than a 100 square foot area with a 50 ppb concentration. There is no currently available hot spot sampling methodology that includes a consideration of concentration as well as size of the hot spots.

6.0 Health Risk Estimates and Hot Spots

The Center for Disease Control (CDC) recently constructed a health risk assessment on exposure of humans to 2,3,7,8-tetrachlorodibenzo-p-dioxin [11]. The assessment estimated that a daily human intake of 28 to 1,428 fg/kg body weight/day poses a risk of one excess lifetime cancer per million persons exposed. Similarly, 276 fg to 14.3 pg/kg b.w./day poses a risk of one excess lifetime cancer per 100,000 persons exposed. By assuming absorption of dioxin from soil via dermal, oral, or respiratory routes, and considering exposure to children in residential areas, CDC declared 1 ppb in soil as the level for concern. CDC recognizes that similar levels of concern may be different for commercial, industrial, or remote areas and for grazing land. These situations must be addressed on a case-by-case basis.

The first six areas to be considered for cleanup are all residential. Figure 5 shows the range of virtually safe doses for soil concentrations as a function of excess cancer risk. Figure 6 shows the average daily dose that would be received if 100, 10, or 1% dioxin at initial soil concentrations were available and estimates the range of 10^{-6} and 10^{-4} cancer risk for a 70-kg person over a 70-year lifetime.

In considering cleanup, these figures provide additional support for the concept of using an average concentration as the criterion for decision and relieves concerns about potential hot spots. If we assume that 1 ppb is the decision level, and if 2% of the area were at 50 ppb, the daily dose would still fall within the 10^{-4} excess lifetime cancer risk range. It is important to emphasize that sampling and analytical procedures are much more precise, within error of 10 to 50%, than the assumptions of the risk assessment which may cover several orders of magnitude. In summary, health risk assessments are based on an average potential exposure to the population and include in their estimation small variations in the concentration of dioxin.

EXCESS LIFETIME RISK OF DEVELOPING CANCER CORRESPONDING TO INITIAL TCDD - SOIL CONTAMINATION LEVELS

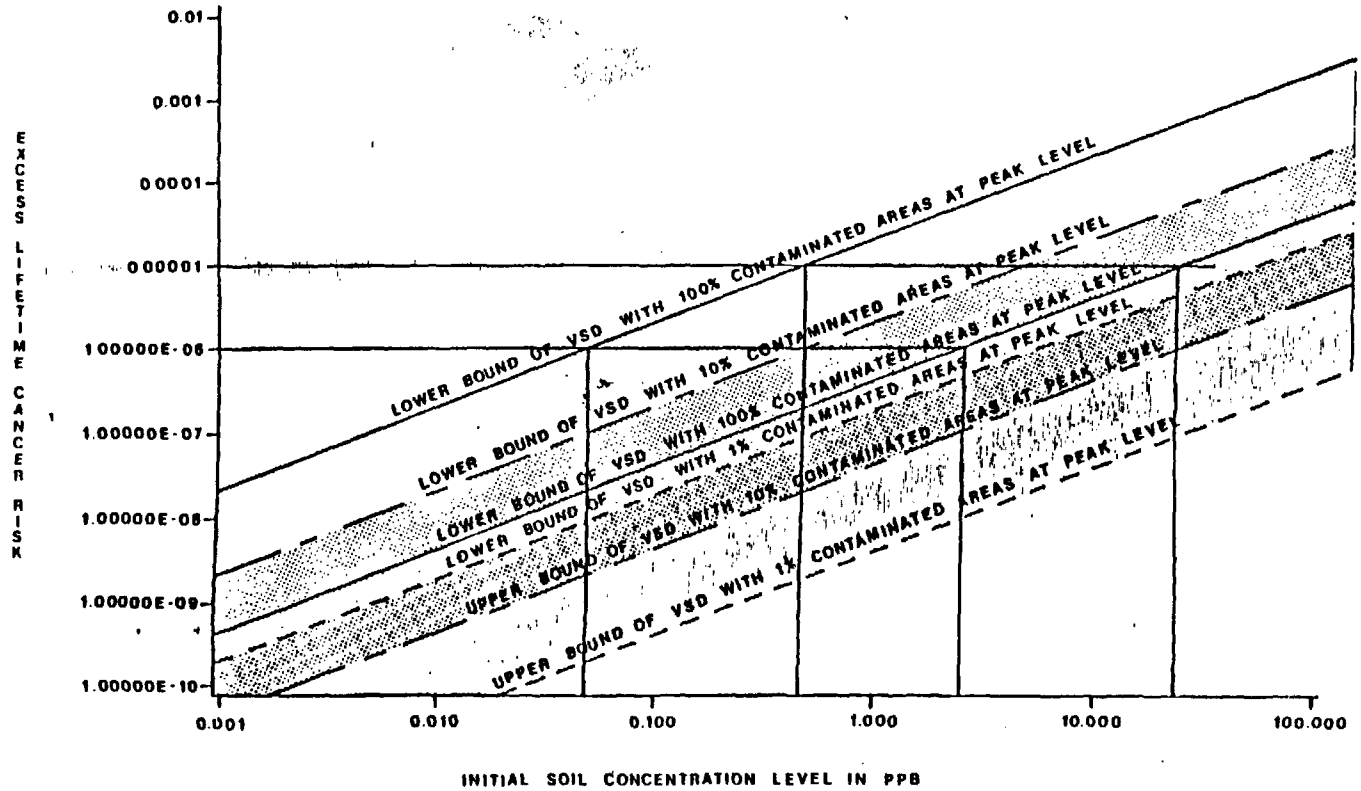


FIGURE 5

ESTIMATED AVERAGE DAILY DOSE CORRESPONDING TO INITIAL TCDD-SOIL CONTAMINATION LEVELS

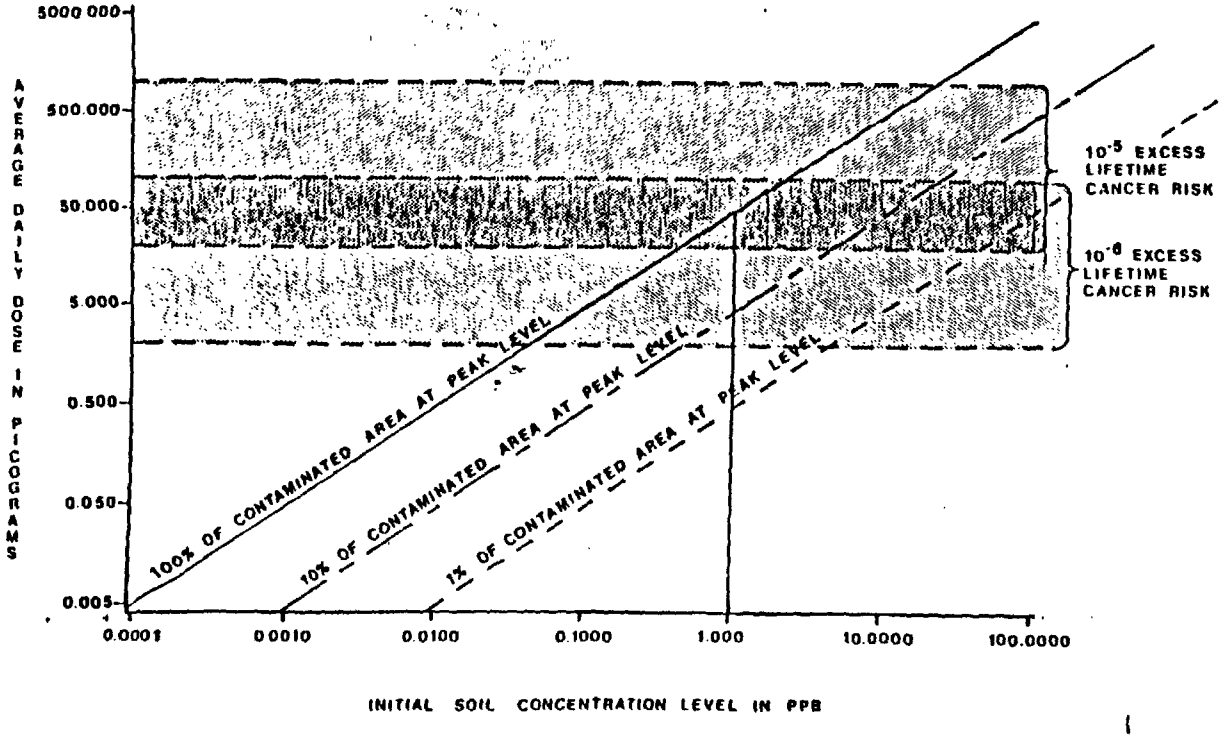


FIGURE 6

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ATTACHMENT 2

RAPID DETERMINATION OF TCDD IN SOIL AND SEDIMENT USING GAS CHROMATOGRAPHY AND TANDEM MASS SPECTROMETRY

ATTACHMENT 2

RAPID DETERMINATION OF TCDD IN SOIL AND SEDIMENT USING GAS CHROMATOGRAPHY AND TANDEM MASS SPECTROMETRY

MARCH 1986

U. S. ENVIRONMENTAL PROTECTION AGENCY

REGION VII

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This method is for use in the rapid determination of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) in soil and sediment, when 2,3,7,8-TCDD is known to be the principal or only tetrachlorodibenzodioxin isomer present. The method is not specific for the 2,3,7,8-TCDD isomer, unless a capillary column which separates that isomer from the other 21 TCDD isomers is employed. The method is applicable in the concentration range of 0.3-25 ug/kg.

The method employs a tandem quadrupole mass spectrometer (MS/MS) as the final detector. The specificity of detection inherent in such a system significantly reduces the need for sample cleanup. This, in turn, improves productivity and cost-effectiveness relative to other high resolution and low resolution GC/MS analysis techniques. The apparatus and methods described are designed for use in a mobile laboratory, which permits on-site analyses.

The method is intended to be used when analytical results are required rapidly, such as when site cleanup operations are in progress. Since the method is not isomer specific, false positives, including isomers other than 2,3,7,8-TCDD, may occur. But errors in this regard would be on the side of safety. Emphasis in the method is placed on avoiding false negatives, as this is a more critical consideration when public health is to be protected.

This method is restricted to use only by or under the supervision of analysts experienced in the use of gas chromatography/triple quadrupole mass spectrometers and skilled in the interpretation of mass spectra.

Because of the extreme toxicity of this compound, the analyst must prevent exposure to himself, or to others, by materials known or believed to contain 2,3,7,8-TCDD. Section IV of this method contains guidelines and protocols that serve as minimum safe-handling standards in a limited access laboratory.

Analyte	CAS Number
2,3,7,8-TCDD	1746-01-6

II. SUMMARY OF METHOD

Five (5) grams of anhydrous sodium sulfate is placed in a 10 ml serum vial and the vial with cap and septum is weighed. Approximately 5 grams of a soil sample is added and the vial is re-weighed. The sample is spiked with internal and surrogate standards of isotopically labelled 2,3,7,8-TCDD. The sample is mixed by shaking, and extracted with acetonitrile/dichloromethane in the closed vial. An aliquot of the extract is taken and, after separation from acetonitrile, the dichloromethane is used directly for GC/MS/MS analysis. Clean-up should usually not be necessary, but a clean-up procedure is included for those samples which do not meet quality assurance criteria. Concentration of the extract may be done to lower the minimum detectable concentration. Capillary column GC/MS/MS conditions are described which allow for separation of TCDD from the bulk sample matrix and measurement of TCDD in the extract.

Quantification is based on the response of native TCDD relative to the isotopically labelled TCDD internal standard. Performance is assessed based on the results for surrogate standard recoveries, EPA performance evaluation samples, spike recovery tests, and method and field blanks.

III. INTERFERENCES

Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing hardware that lead to discrete artifacts and/or elevated backgrounds at the ions monitored. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory method blanks as described in Section VIII.

The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the sample. 2,3,7,8-TCDD is often associated with other interfering chlorinated compounds which are at concentrations several magnitudes higher than that of 2,3,7,8-TCDD.

The use of a triple quadrupole mass spectrometer as the detector serves to minimize the influence of many of these interferents.

IV. SAFETY

The following safety practices are excerpted directly from EPA Method 613, Section 4 (July 1982 version): See following page.

treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are identified[8-10]. Benzene and 2,3,7,8-TCDD have been identified as suspected human or mammalian carcinogens.

4.2 Each laboratory must develop a strict safety program for handling of 2,3,7,8-TCDD. The following laboratory practices are recommended:

4.2.1 Contamination of the laboratory will be minimized by conducting all manipulations in a hood.

4.2.2 The effluents of sample splitters for the gas chromatograph and roughing pumps on the GC/MS should pass through either a column of activated charcoal or be bubbled through a trap containing oil or high-boiling alcohols.

4.2.3 Liquid waste should be dissolved in methanol or ethanol and irradiated with ultraviolet light with wavelength greater than 290 nm for several days. (Use F40BL lamps or equivalent.) Analyze liquid wastes and dispose of the solutions when 2,3,7,8-TCDD can no longer be detected.

4.3 Dow Chemical U.S.A. has issued the following precautions (revised 11/78) for safe handling of 2,3,7,8-TCDD in the laboratory:

4.3.1 The following statements on safe handling are as complete as possible on the basis of available toxicological information. The precautions for safe handling and use are necessarily general in nature since detailed, specific recommendations can be made only for the particular exposure and circumstances of each individual use. Inquiries about specific operations or uses may be addressed to the Dow Chemical Company. Assistance in evaluating the health hazards of particular plant conditions may be obtained from certain consulting laboratories and from State Departments of Health or of Labor, many of which have an industrial health service. 2,3,7,8-TCDD is extremely toxic to

been handled for years without injury in analytical and biological laboratories. Techniques used in handling radioactive and infectious materials are applicable to 2,3,7,8-TCDD.

4.3.1.1 Protective Equipment: Throw-away plastic gloves, apron or lab coat, safety glasses and lab hood adequate for radioactive work.

4.3.1.2 Training: Workers must be trained in the proper method of removing of contaminated gloves and clothing without contacting the exterior surfaces.

4.3.1.3 Personal Hygiene: Thorough washing of hands and forearms after each manipulation and before breaks (coffee, lunch, and shift).

4.3.1.4 Confinement: Isolated work area, posted with signs, segregated glassware and tools, plastic-backed absorbent paper on benchtops.

4.3.1.5 Waste: Good technique includes minimizing contaminated waste. Plastic bag liners should be used in waste cans. Janitors must be trained in safe handling of waste.

4.3.1.6 Disposal of Wastes: 2,3,7,8-TCDD decomposes above 800 °C. Low-level waste such as the absorbent paper, tissues, animal remains and plastic gloves may be burned in a good incinerator. Gross quantities (milligrams) should be packaged securely and disposed through commercial or governmental channels which are capable of handling high-level radioactive wastes or extremely toxic wastes. Liquids should be allowed to evaporate in a good hood and in a disposable container. Residues may then be handled as above.

4.3.1.7 Decontamination: Personal—any mild soap with plenty of scrubbing action. Glassware, Tools, and Surfaces—Chlorothene NU Solvent (Trademark of the Dow Chemical Company) is the least toxic solvent shown to be effective. Satisfactory cleaning may be accomplished by rinsing with Chlorothene, then washing with any detergent and water. Dish water may be disposed to the sewer. It is prudent to minimize solvent wastes because they may require special disposal through commercial sources which are expensive.

4.3.1.8 Laundry: Clothing known to be contaminated should be disposed with the precautions described under "Disposal of Wastes." Lab coats or other clothing worn in 2,3,7,8-TCDD

should be collected in plastic bags. Persons who convey the bags and launder the clothing should be advised of the hazard and trained in proper handling. The clothing may be put into a washer without contact if the launderer knows the problem. The washer should be run through a cycle before being used again for other clothing.

4.3.1.9 Wipe Tests: A useful method of determining cleanliness of work surfaces and tool is to wipe the surface with a piece of filter paper. Extraction and analysis by gas chromatography can achieve a limit of sensitivity of 0.1 µg per wipe. Less than 1 µg 2,3,7,8-TCDD per sample indicates acceptable cleanliness, anything higher warrants further cleaning. More than 10 µg on a wipe sample indicates an acute hazard and requires prompt cleaning before further use of the equipment or work space and indicates further that unacceptable work practices have been employed in the past.

4.3.1.10 Inhalation: Any procedure that may produce airborne contamination must be done with good ventilation. Gross losses to a ventilation system must not be allowed. Handling of the dilute solutions normally used in analytical and animal work presents no inhalation hazards except in case of an accident.

4.3.1.11 Accidents: Remove contaminated clothing immediately, taking precautions not to contaminate skin or other articles. Wash exposed skin vigorously and repeatedly until medical attention is obtained.

019012

V. APPARATUS AND MATERIALS

All glassware is initially cleaned with aqueous detergent and then rinsed with tap water, deionized water, acetone, toluene and methylene chloride. Other cleaning procedures may be used as long as acceptable method blanks are obtained.

Electronic balance, capable of weighing at least 50 g, with an accuracy of at least ± 0.05 g.

Shaker, vortex-type or equivalent

Centrifuge, 4000 rpm, capable of handling 25 mm diameter vials

Centrifuge tubes

10 ml serum vials; with teflon faced septa and aluminum caps (Chrompak 10204 and 10213 or equivalent)

1 ml serum vials; with teflon faced septa and aluminum caps (Chrompak 10201 and 10211 or equivalent)

Crimper for 10 ml serum vial (Chrompak 10233 or equivalent)

Crimper for 1 ml serum vial (Chrompak 10231 or equivalent)

Disposable teflon 0.45 micron filters (Millipore SLHV025 HB, or equivalent)

5 ml disposable Glaspak syringes (Sargent Welch S-79401-B or equivalent)

18 gauge disposable syringe needle (Sargent Welch S-79402-G or equivalent)

Disposable pipets, 5 3/4 inches x 7 mm o.d.

Glass wool, silanized

Nitrogen blowdown apparatus

Gas chromatograph - an analytical system with all required accessories including syringes and analytical columns. The injection port must be designed for capillary columns and splitless injection.

Triple quadrupole mass spectrometer with GC transfer line and glow discharge ion source (TAGA® 6000, SCIEX©, Thornhill, Ontario, Canada)

Compressed Gases: Zero Grade Air (from distillation, not water hydrolysis)
Ultra High Purity Nitrogen
Ultra High Purity Argon

Column: 15 m long, wide bore fused silica capillary (eg. 0.32 mm I.D.)
DB-5 1.0 micron film thickness.

VI. REAGENTS

Stock Standard Solutions

Stock standard solutions correspond to three toluene solutions containing unlabelled 2,3,7,8-TCDD at varying concentrations, and $^{13}C_{12}$-2,3,7,8-TCDD (internal standard, CASRN 80494-19-5) at a constant concentration. These solutions also contain $^{37}Cl_4$-2,3,7,8-TCDD (surrogate compound, CASRN 85508-50-5) at varying concentrations. These stock solutions are to be used in preparing the calibration standard solutions, and are to be obtained from the Quality Assurance Division, USEPA, Environmental Monitoring Systems Laboratory (EMSL-LV), Las Vegas, Nevada. If not available from EMSL-LV, stock standard solutions may be prepared from commercially available standards. However, the accuracy of these solutions must be checked against EPA supplied standard solutions.

019014

The three stock solutions will have the following concentrations of unlabelled, internal and surrogate standards.

Stock Solution #1 (CC1)

Unlabeled 2,3,7,8-TCDD - 0.2 ng/ul
$^{13}C_{12}$-2,3,7,8-TCDD - 1.0 ng/ul
$^{37}Cl_4$-2,3,7,8-TCDD - 0.06 ng/ul

Stock Solution #2 (CC2)

Unlabeled 2,3,7,8-TCDD - 1.0 ng/ul
$^{13}C_{12}$-2,3,7,8-TCDD - 1.0 ng/ul
$^{37}Cl_4$-2,3,7,8-TCDD - 0.12 ng/ul

Stock Solution #3 (CC3)

Unlabeled 2,3,7,8-TCDD - 5.0 ng/ul
$^{13}C_{12}$-2,3,7,8-TCDD - 1.0 ng/ul
$^{37}Cl_4$-2,3,7,8-TCDD - 0.2 ng/ul

NOTE: Store stock solutions in 1 ml amber mini-vials under refrigeration.

Calibration Standard Solutions

Calibration standard solutions are prepared to simulate the conditions of sample analysis as nearly as possible. Three calibration standard solutions are prepared from the stock standard solutions so as to contain constant amounts of internal standard (5 ug/kg equivalent) with variable amounts of unlabeled standard (1,5, and 25 ug/kg equivalent) and surrogate standard (0.3, 0.6, and 1.0 ug/kg equivalent). The equivalent concentrations are based on the use of 5-gram samples, extraction with 5 ml of 2:1 acetonitrile: dichloromethane, and a final extract volume of approximately 1.66 ml dichloromethane after removal of acetonitrile, as called for in the procedure.

Low Level

Add 750 ul of stock solution #1 to a 5 ml volumetric flask and bring to volume with dichloromethane. Mix well. This solution contains an equivalent concentration of 1 ug/kg of 2,3,7,8-TCDD, 5 ug/kg of $^{13}C_{12}$-2,3,7,8-TCDD, and 0.3 ug/kg of $^{37}Cl_4$-2,3,7,8-TCDD.

Medium Level

Add 750 ul of stock solution #2 to a 5 ml volumetric flask and bring to volume with dichloromethane. Mix well. This solution contains an equivalent concentration of 5 ug/kg of 2,3,7,8-TCDD, 5 ug/kg of $^{13}C_{12}$-2,3,7,8-TCDD, and 0.6 ug/kg of $^{37}Cl_4$-2,3,7,8-TCDD.

High Level

Add 750 ul of stock solution #3 to a 5 ml volumetric flask and bring to volume with dichloromethane. Mix well. This solution contains an equivalent concentration of 25 ug/kg of 2,3,7,8-TCDD, 5 ug/kg of $^{13}C_{12}$-2,3,7,8-TCDD, and 1.0 ug/kg of $^{37}Cl_4$-2,3,7,8-TCDD.

NOTE 1: Although the surrogate, $^{37}Cl_4$-2,3,7,8-TCDD, is present in all three level calibration solutions, only the high level solution is used for calculating the relative response factor for the surrogate.

NOTE 2: All calibration standard solutions must be stored in an isolated refrigerator and protected from light. Check these standard solutions frequently for signs of evaporation.

Sample Spiking Solution

The sample spiking solution is also to be obtained from the Quality Assurance Division, U. S. EPA Environmental Monitoring Systems Laboratory (EMSL-LV), Las Vegas, Nevada. The spiking solution will have the following concentrations of internal and surrogate standards.

$^{13}C_{12}$-2,3,7,8-TCDD - 0.5 ng/ul
$^{37}Cl_4$-2,3,7,8-TCDD - 0.1 ng/ul

When 50 ul of this solution is spiked in 5 g of soil, the resulting concentrations in the soil are 5 ug/kg and 1 ug/kg of internal and surrogate standard, respectively.

It is recommended that approximately 2.5-5 ml of the spiking solution be transferred to a 5 ml serum vial and sealed with a septum and cap prior to each day's work for use in spiking samples that day.

NOTE: It is very important that no evaporation of sample spiking solution be allowed to occur, since the accuracy of results are directly dependent on the addition of a known amount of internal standard.

Field Blank Spiking Solution

The field blank spiking solution is also to be obtained from the Quality Assurance Division, U. S. EPA, Environmental Monitoring Systems Laboratory (EMSL-LV), Las Vegas, Nevada. The spiking solution will have the following concentrations of unlabelled, internal, and surrogate standards:

2,3,7,8-TCDD - 0.1 ng/ul
$^{13}C_{12}$-2,3,7,8-TCDD - 0.5 ng/ul
$^{37}Cl_4$-2,3,7,8-TCDD - 0.1 ng/ul

When 50 ul of this solution is spiked in 5 grams of soil, the resulting concentrations in the soil are 5 ug/kg of internal standard and 1 ug/kg each of unlabelled and surrogate standard.

NOTE: It is very important that no evaporation of field blank spiking solution be allowed to occur, since the accuracy of results are directly dependent on the addition of a known amount of internal standard.

Solvent

All solvents should be pesticide grade or equivalent. The following solvents will be needed:

Acetonitrile
Dichloromethane
Cyclohexane
Toluene
Benzene
Methanol

Silica Gel

Type 60, 70-230 mesh. Soxhlet extracted with dichloromethane for 24 hours, then activated for 24 hours at 130°C.

Acid Alumina

AG 4, 100-200 mesh. soxhlet extracted with dichloromethane for 24 hours, then activated for 24 hours at 190°C.

Carbopack C

Celite 545

Sodium Sulfate

(ACS) granular, anhydrous.

VII. CALIBRATION AND LIMIT OF DETECTION DETERMINATIONS

Calibration must be done using the internal standard technique. In this case, the internal standard is an isotope of the compound-of-interest, and

metry. The three calibration standard solutions described in section VI are required.

Inject 1-2 ul of each of the calibration standard solutions and acquire selected reaction monitoring data for the following parent- daughter ions:

m/z = 320 →257
m/z = 322 →259
m/z = 328 →263
m/z = 332 →268

For simplicity in subsequent sections, we will refer only to the daughter ions, since quantitation is based on daughter ion response.

Relative response factors for unlabelled 2,3,7,8-TCDD vs the internal standard for triplicate determinations of each of the three calibration standard solutions are calculated.

Equation I: Relative Response Factor (RRFs) for 2,3,7,8-TCDD

$$RRFs = (A_s C_{is})/(A_{is} C_s)$$

where A_s = the sum of the area responses for the ions, m/z 257 and 259, corresponding to the unlabelled standard, 2,3,7,8-TCDD.

A_{is} = the area response of the ion m/z 268, corresponding to the internal standard, $^{13}C_{12}$-2,3,7,8-TCDD.

C_s = the concentration of the unlabelled standard, 2,3,7,8-TCDD

C_{is} = the concentration of the internal standard, $^{13}C_{12}$-2,3,7,8-TCDD.

In the case of the unlabelled 2,3,7,8-TCDD each of the calibration standard solutions must be analyzed in triplicate, and the variation of the RRF values for each compound at each concentration level must not exceed 10% RSD. If the three mean RRF values for each compound do not differ by more than ± 10%, the RRF can be considered to be independent of analyte quantity for the calibration concentration range, and the mean of the three mean RRFs shall be used for concentration calculations. The overall mean is termed a calibration factor.

Similarly, relative response factors for the surrogate standard vs the internal standard for the triplicate determinations of the high level calibration solution are also calculated.

Equation II: Relative Response Factor (RRF_{ss}) for $^{37}Cl_4$-2,3,7,8-TCDD

$$RRF_{ss} = (A_{ss} C_{is})/(A_{is} C_{ss})$$

where A_{ss} = the area response of the daughter ion, m/z 263, corresponding to the surrogate standard, $^{37}Cl_4$-2,3,7,8-TCDD.*

* Subtract 0.0108 of any 257 response from the 263 response to correct for contributions of 2,3,7,8-TCDD to the 263 response.

A_{is} = the area response of the ion m/z 268, corresponding to the internal standard, $^{13}C_{12}$-2,3,7,8-TCDD.

C_{ss} = the concentration of the surrogate standard, $^{37}Cl_4$-2,3,7,8-TCDD.

and C_{is} = the concentration of the internal standard, $^{13}C_{12}$-2,3,7,8-TCDD.

In the case of the surrogate standard, $^{37}Cl_4$-2,3,7,8-TCDD, the variation of the three RRF values for the high level calibration solution should not exceed 10% RSD. If this is the case, the mean of the three RRFs shall be used for concentration calculations. The overall mean is termed a calibration factor.

The calibration factor for the unlabelled 2,3,7,8-TCDD must be verified on each work shift of 8 hours or less by the analysis of a low level calibration standard. If the RRF for the low level calibration differs from the calibration factor by more than 10%, the entire calibration must be repeated and a new calibration factor determined. The most recently verified calibration factor must be used in all calculations. This verification is only required for the unlabelled standards. There is no need to check the surrogate calibration factor unless the surrogate recoveries appear biased or consistently fall outside the 60-140% control limits.

The theoretical ratio of the m/z 257 to 259 ions for native 2,3,7,8-TCDD is 1.02. However, in practice this ratio will differ from the theoretical due to the very low resolution used in both analyzing quadrupoles for this type of analysis. The ratio must therefore, be determined empirically as follows:

Equation III: (Ratio of native TCDD daughter ions)

$$\text{Ratio} = A_{257}/A_{259}$$

where A_{257} = Area response for ion m/z 257

A_{259} = Area response for ion m/z 259

The mean of the ratios calculated for each of the nine calibration solutions is used for comparison purposes for qualitative identification of 2,3,7,8-TCDD.

It has been found that the sample spiking solution also gives responses for the 257 and 259 daughter ions corresponding to 2,3,7,8-TCDD. These contributions must be subtracted out for each sample. In order to determine this correction factor, add 150 ul of the sample spiking solution to a 5 ml volumetric flask and bring to volume with dichloromethane. Twenty 1-2 ul injections of this solution must be made and the ratio of the area responses for the sum of the m/z 257 and 259 ions vs the m/z 268 ion must be calculated. Twenty separate ratios must be determined.

Equation IV: Blank Response (B) of Sample Spiking Solution

$$B = A_b/A_{is}$$

where A_b = the sum of the area responses for the ions, m/z 257 and 259, obtained with the spiking solution

and A_{is} = The area response of the ion m/z 268, corresponding to the internal standard $^{13}C_{12}$-2,3,7,8-TCDD present in the spiking solution.

The correction factor for the blank contribution to sample response is then calculated as the mean of the 20 blank responses.

Equation V: Correction Factor (C.F.) for Blank Contribution

$$C.F. = \frac{\Sigma B}{n}$$

where ΣB = The sum of the individual blank responses determined by Equation IV.

n = Number of replicate measurements of the blank response (20 are required for initial determination).

Limit Of Detection

The empirical limit of detection will be calculated based on the variability of the blank responses. The blank responses correspond to those obtained from repeat injections of the (diluted) sample spiking solution. Each blank response must be converted to an equivalent concentration of 2,3,7,8-TCDD.

Equation VI: (Conversion of Blank Response to An Equivalent Concentration of 2,3,7,8-TCDD)

$$C_b = \frac{A_b \times Q_{is}}{A_{is} \times RRF_s \times W} = \frac{25 \times A_b}{5 \times A_{is} \times RRF_s}$$

where C_b = equivalent concentration of 2,3,7,8-TCDD in blank (spiking solution) (in units of ug/kg or ppb)

A_b = the sum of the area responses of the ions m/z 257 and 259 for the blank

A_{is} = the area response of the ion m/z 268, corresponding to the internal standard

RRF_s = The relative response factor previously determined for 2,3,7,8-TCDD (Equation I)

Q_{is} = 25 nanograms (the weight of internal standard added to each sample)

W = 5 grams (the weight of wet soil used for each sample)

The standard deviation of the blank responses (in concentration units) must then be calculated.

Equation VII: (Standard Deviation of The Blank Responses)

$$S_b = \frac{(\Sigma C_b^2) - (\Sigma C_b)^2/n}{n-1}$$

where S_b = standard deviation of the blank responses (in units of ug/kg)

C_b = blank response in concentration units (calculated using Equation VI)

n = number of replicate blank results used (20 are required)

Finally, the limit of detection must be calculated from the standard deviation of the blank.

Equation VIII: (Limit of Detection Based on "Well-Known" Blank)*

$$LOD = 2\ t\ S_b$$

where LOD = Limit of Detection

t = the 10% point of the t statistic for a double-sided table with n-1 degrees of freedom (where n is equal to the number of blank results used). NOTE: The LOD must be calculated based on at least 20 replicate blank (i.e. spiking solution) analyses. For n = 20, t = 1.72.

The limit of detection calculated from equation VIII should be less than the required limit of detection of 0.3 ug/kg.

VIII. QUALITY CONTROL REQUIREMENTS

The following quality control (Q.C.) requirements are listed in the order that they must be run. Requirements 1 and 2 are to be run initially before any other samples. Requirements 3 through 7 are the Q.C. samples to be included with each batch of real samples (requirement #8) that is run in one 8-hour time period or on each shift. The requirements 3 through 8 are to be run in the order as they appear in the list below on each shift.

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* Reference - Currie, Lloyd A. "Limits for Qualitative Detection and Quantitative Determination" Anal, Chem., 40, 3, 586-593, 1968

1. An initial calibration must be performed using calibration standard solutions with varied (1,5, and 25 ug/kg equivalent) native TCDD and 5 ug/kg equivalent internal standard. Calibration for the surrogate standard will be based only on the high level standard (1 ug/kg equivalent). The criteria given in Section VII must be met or the calibration must be repeated.

2. Initially, 20 replicate determinations of the spiking solution must be run and area responses for the sum of m/z 257 and 259 ions vs the m/z 268 ion must be calculated. Twenty separate ratios must be determined (Equation IV) and used in calculating the mean correction factor (Equation V).

3. A 1-point check verification using the 1 ug/kg equivalent native TCDD and 5 ug/kg equivalent internal standard must be run once every 8 hours or on every shift. If the RRF values from this calibration check differ by more than $\pm$ 10% from the previously determined mean relative response factor (RRFs), the 3-point calibration must be repeated. The calibration check for the surrogate is not necessary unless the surrogate recoveries appear biased and/or consistently fall outside the 60-140% control limits.

4. A laboratory "method blank" must be run along with each batch of 24 or fewer samples. A method blank is performed by executing all of the specified extraction steps, except for the introduction of a 5 gram sample. The method blank is also dosed with the internal standard and surrogate standard. Results for the method blank must be calculated the same way as samples. This includes correction for the spiking solution contribution as indicated in Equation IX. A positive response $\geq$ 0.3 ug/kg of native TCDD followed by reinjection. If still positive, re-extraction and reanalysis of all related samples must be done.

5. "Field blanks" will be provided to monitor for possible cross-contamination of samples in the lab. The "field blank" will consist of uncontaminated soil (background soil taken off-site). A positive response $\geq$ 0.3 ug/kg native TCDD must be followed by reinjection. If still positive, all samples associated with the field blanks must be re-extracted and reanalyzed.

6. One sample, designated by EPA, must be spiked with native 2,3,7,8-TCDD at a level of 1 ug/kg for each set of 24 or fewer samples. The Field Blank Spiking Solution (Section VI) should be used to spike the designated sample. The recovery must be 0.6 to 1.4 ug/kg or the analysis stopped and all related samples must be re-extracted and reanalyzed.

7. The laboratory will be given performance evaluation samples by EPA to run with each batch of samples. The results from these performance evaluation samples will be evaluated by EPA. If a result is not within the acceptance criteria set by EPA, all samples in the batch associated with that PE sample must be reanalyzed.

8. Each sample must be dosed with 50 ul of the sample spiking solution containing internal standard (equivalent to 5.0 ug/kg) and surrogate standard (equivalent to 1.0 ug/kg). The surrogate recovery must be 0.6 to 1.4 ug/kg or the sample must be reanalyzed.

9. The following qualitative requirements must be met in order to confirm the presence of native 2,3,7,8-TCDD:

a. The retention time must equal (within 3 seconds) the retention time for the internal standard.

b. The 257/259 ratio must be within the range ± 10% of the value of the ratio determined in Section VII, (Equation III).

c. The ion responses at 257 and 259 must be present and maximize together. The signal to mean noise ratio must be 2.5 to 1 or better for both daughter ions. (Determine the noise level by measuring the random peak to valley signal present on either side [within 20 scans] of the 2,3,7,8-TCDD retention window. The 2,3,7,8-TCDD signal must be at least 2.5 times larger than this.)

d. For those samples giving non-detect results, the result must be less than the 0.3 ug/kg required limit of detection. Otherwise the analysis must be stopped and interferences identified and corrected until the 0.3 ug/kg required limit of detection is met.

e. For each sample, the internal standard must be present with at least a 10 to 1 signal to noise ratio based on the m/z 268 ion response.

IX. SAMPLE COLLECTION, PRESERVATION AND HANDLING

The procedures for sample collection, shipping and handling will be specified by the EPA Regional Office responsible for the monitoring exercise. The sampling team will be provided with an 8 ounce glass jar, and 30-300 grams of soil will be collected. When received in the laboratory, the sample should be thoroughly mixed in the jar for a minimum of 3 minutes, using a stainless steel spatula. The spatula should be used to break up large clumps of soil while mixing to achieve a homogeneous sample.

A 5 gram aliquot sample should be taken and placed in a pre-weighed 10 ml serum vial containing approximately 5 grams of anhydrous sodium sulfate together with a Teflon-faced septum and cap (The entire vial, Na_2SO_4, septum and cap is pre-weighed and labelled). The 5 gram aliquot sample should be representative of the entire sample. Thus, large stones or other particles which are uncharacteristic of the sample, should not be included in the aliquot.

Samples may be stored under ambient conditions as long as temperature extremes (below freezing or above 90°F) are avoided. Samples must be protected from light to avoid photodecomposition.

All samples must be extracted and completely analyzed within 24 hours. Extracts must be held for 6 months prior to disposal.

CAUTION: Although the sample and standards are sealed throughout the extraction procedure, there is always the possibility of leakage and breakage (especially during the sample spiking and centrifuging steps). The analyst should, therefore, be fully protected by wearing plastic gloves and laboratory jacket (a face protector is optional). See Section IV for details on specific safety requirements.

1. Prepare extraction solvent by mixing two volumes acetonitrile with one volume dichloromethane. Mix solvents thoroughly.

2. Weigh the sample vial and determine the net weight of sample (to 3 significant figures).

3. Add 50 ul of the sample spiking solution (containing both internal and surrogate standards). The solution will contain 0.5 ng/ul of internal standard and 0.1 ng/ul of surrogate standard. Add the 50 ul solution directly to the soil, spreading it over several sites on the surface of the soil.

4. Attempt to mix the soil and sodium sulfate by shaking. (Extremely wet samples may not mix well, but DO NOT open the vial to stir the contents.) Additional anhydrous sodium sulfate should be added if needed.

5. Pierce the septum with a disposable needle and leave the needle in place to vent the contents while the extraction solvent is introduced.

6. Add 5 ml of the 2:1 acetonitrile: dichloromethane extraction solvent using a 5 ml syringe and disposable needle. Retain the syringe for solvent additions only.

NOTE: Additional extraction solvent can be added if the analyst judges this necessary to achieve efficient extraction on a particular sample.

7. Remove the syringe and both needles (they should be treated as though contaminated). Dispose of both needles.

8. Shake the vial vigorously on a vortex mixer for 2 minutes.

9. Centrifuge the vial and contents at 4000 rpm for 2 minutes. Remove carefully so as not to disturb the sediment.

10. Insert a needle through the septum so that it just breaks the surface of the septum inside the vial. Using a clean disposable syringe and needle, withdraw approximately 1 ml of the extract; NOTE: The other needle through the septum serves to equilibrate the pressure upon withdrawal of the extract.

11. Invert the syringe and withdraw the plunger to remove the extract from the needle. Dispose of the needle (it is contaminated).

12. Place a 0.45 micron disposable Teflon filter on the syringe and inject the extract into a clean 10 ml serum vial containing 9 ml distilled water. Dispose of the syringe and the filter.

13. Using a Teflon lined septum and an aluminum cap, cover and crimp the vial containing the water-extract mixture.

14. Manually shake the vial vigorously for about one minute.

15. Centrifuge the vial to separate the dichloromethane phase from the water/acetonitrile phase. The dichloromethane phase will appear as a small bubble at the bottom of the vial.

16. Prepare a miniature drying tube as follows:

a. Plug the tip of a disposable pipet with a small amount of silanized glass wool.

b. Add approximately 1/2 cm anhydrous sodium sulfate.

17. With a disposable syringe and needle, remove the dichloromethane phase from the vial (step 15) as completely as possible.

18. Transfer the dichloromethane phase through the drying tube into a clean 1 ml serum vial.

19. Rinse the drying tube with one-half ml dichloromethane, and collect in the same 1 ml serum vial.

20. Under a stream of nitrogen, evaporate the solvent gently until the volume of solution remaining in the serum vial is 0.05-0.1 ml.

21. Seal the 1 ml serum vial with a Teflon lined septum and cap. Label the vial appropriately.

XI. CLEANUP

The need for cleanup is indicated when a particular extract does not meet the QC criteria for the coelution of all four monitored ions, surrogate recovery, or the ratio A_{257}/A_{259}. Two cleanup procedures are given below.

A. Modified Option A Cleanup

1. Plug the tip of a disposable pipet with a small amount of silanized glass wool.

2. Place approximately a 1 cm layer of silica gel over the glass wool.

3. Place approximately a one-half cm layer of anhydrous sodium sulfate over the silica gel.

4. Plug the tip of a second disposable pipet with a small amount of silanized glass wool.

5. Place approximately 0.5 cm acid alumina over the silanized glass wool.

6. Place approximately 0.5 cm anhydrous sodium sulfate over the alumina.

7. Arrange the two columns so that the silica gel column will elute onto the alumina column, and the alumina column drippings will be collected in a vial.

8. Rinse the two columns with 0.5 ml cyclohexane and discard the eluate.

9. Open the vial containing the extract and add 1 ml cyclohexane to the extract.

10. Under a stream of nitrogen, carefully evaporate the dichloromethane from the extract vial (the volume of the remaining solution should be just under 1 ml).

11. Transfer the entire contents of the extract vial onto the silica column, arranged as specified in step 7.

12. When the solution just reaches the surface of the sodium sulfate layer in the silica gel column, add 0.5 ml cyclohexane.

13. Repeat step 12 a second time. Allow the solution to drip completely after the second addition of cyclohexane.

14. Discard the silica gel column.

15. Rinse the alumina column with an additional 1 ml cyclohexane. Discard the accumulated eluates in the vial beneath the column.

16. Place a clean 1 ml serum vial under the alumina column.

17. Elute the alumina column with three successive portions of 0.5 ml each of 15% by volume dichloromethane in cyclohexane, collecting the eluate in the clean vial.

18. With gentle heating and under a stream of nitrogen, evaporate the solvent until the volume in the vial is 0.05-0.1 ml.

19. Seal the serum vial with a teflon lined septum and cap. Label the vial appropriately. NOTE: If it is a priori known that the second step of cleanup is required, evaporate the sample in stage 18 to just below 1 ml and immediately proceed with a second cleanup as described below.

B. Option D Cleanup

All samples indicating the presence of other TCDD isomers or which contain compounds co-elerting must be cleaned up using Option D.

1. In advance, prepare a mixture of 3.6 g Carbopack C with 16.4 g Celite 545. Activate the mixture at 130°C for 6 hours.

2. Plug the tip of a disposable pipet with a small amount of silanized glass wool.

3. Place 2 cm layer of the carbopack-Celite mixture over the glass wool plug, using suction to pack the column.

4. Rinse the column sequentially with 2 ml toluene, 1 ml dichloromethane-methanol-benzene (75:20:5 by volume), 1 ml cyclohexane-dichloromethane 1:1 by volume), and finally 2 ml cyclohexane. Collect the eluate in a vial and discard the eluate.

5. Dilute the extract which has been cleaned up by the Modified Option A procedure to 1 ml with cyclohexane.

6. Maintaining a discard vial under the column, introduce the extract onto the column.

7. After the solvent has drained, rinse the column successively with 2 ml cyclohexane, 1 ml cyclohexane-dichloromethane mixture (1:1 by volume) and 1 ml dichloromethane-methanol-benzene mixture (75:20:5 by volume).

8. Allow the column to drain completely and discard the accumulated eluates.

9. Place a clean serum vial under the column.

10. Elute the dioxin from the charcoal with 2 ml toluene.

11. With gentle heating and under a stream of nitrogen, concentrate the extract to a volume of 0.05-0.1 ml.

12. Seal the serum vial with a Teflon lined septum and cap. Label appropriately.

XII. GC/MS/MS ANALYSIS

1. Table 1 summarizes the 15 m DB-5 gas chromatographic capillary column and operating conditions. The 15 m DB-5 column has been used for chromatography which is not isomer specific (no valley is observed between the 1,2,3,4-TCDD and 2,3,7,8-TCDD isomers).

2. Standards and samples must be analyzed under identical MS/MS conditions. Selected Reaction Monitoring (SRM) scans are used, using a scan time to give at least five points per chromatographic peak. Recommended MS/MS conditions are given in Table 2.

3. Verify the Calibration of the system daily as described in Section VII. The volume of calibration standard injected should be approximately the same as all sample injection volumes. The requirements described in Section VIII, Parts 9b and 9c must be met for all calibration standards.

4. Inject a 1 to 2 ul aliquot of the sample extract.

5. The presence of TCDD is qualitatively confirmed if the criteria of Section VIII, Part 9, are achieved.

6. For quantitation, measure the area response of the m/z 257 and 259 peaks for 2,3,7,8-TCDD; the m/z 268 peak for $^{13}C_{12}$-2,3,7,8-TCDD, and the m/z 263 peak for $^{37}Cl_4$-2,3,7,8-TCDD. Calculate the concentrations of native and surrogate standards using the following equations:

$$C_s = \frac{((A_s/A_{is}) - C.F.)\ (Q_{is})}{RRFs \times W}$$

where C_s = The concentration of native 2,3,7,8-TCDD in ug/kg

A_s = the sum of the area responses for the ions, m/z 257 and 259

A_{is} = the area response for the ion m/z 268

C.F. = correction factor for spiking solution (blank) previously determined (Equation V)

Q_{is} = quantity (in nanograms) of $^{13}C_{12}$-2,3,7,8-TCDD added to the sample before extraction

RRF_s = Relative response factor for 2,3,7,8-TCDD calculated previously (Equation I)

W = weight (in grams) of wet soil or sediment sample.

In evaluating the results, a distinction must be made between quantitative measurement and qualitative identification of 2,3,7,8-TCDD. The following steps must be followed in the treatment of all sample results:

1. Calculate the concentration of native 2,3,7,8-TCDD using equation IX.

2. Determine if all of the qualitative identification criteria are met.

3. If all qualitative identification criteria are met, report the concentration found by equation IX, regardless of concentration.

4. If the qualitative identification criteria are not met, and the concentration calculated by equation IX is less than the required limit of detection of 0.3 ug/kg, report the concentration as less than 0.3 ug/kg (i.e. <0.3 ug/kg).

5. If the qualitative identification criteria are not met, and the concentration calculated by equation IX is greater than the required limit of detection of 0.3 ug/kg, the extract must be reinjected. If the qualitative identification criteria are still not met and the result is still greater than 0.3 ug/kg, the extract must be cleaned up or the sample reanalyzed until a satisfactory result is obtained. (i.e. positive result or negative result below 0.3 ug/kg).

NOTE: In reporting results for sample analysis, a comparison is made with the required limit of detection. The limit of detection based on the blank (Equation VIII) might also be used, but interferences may be present and introduce false positives in some cases. However, as explained in Section VII, the empirical limit of detection based on the blank must be less than the required limit of detection of 0.3 ug/kg.

Equation X: (Calculation of concentration of surrogate standard, $^{37}Cl_4$-2,3,7,8-TCDD)

$$C_{ss} = \frac{A_{ss} \times Q_{is}}{A_{is} \times RRF_{ss} \times W}$$

where C_{ss} = the concentration of surrogate standard $^{37}Cl_4$-2,3,7,8-TCDD in ug/kg.

A_{ss} = the area response for the ion m/z 263*

A_{is} = the area response for the ion m/z 268

Q_{is} = quantity (in nanograms) of $^{13}C_{12}$-2,3,7,8-TCDD added to the sample before extraction.

RRF_{ss} = Relative response factor for $^{37}Cl_4$-2,3,7,8-TCDD calculated previously (Equation II).

W = Weight (in grams) of wet soil or sediment sample.

* Subtract 0.0108 of any 257 response from the 263 response to correct for contributions of any 2,3,7,8-TCDD to the 263 response.

Native 2,3,7,8-TCDD contains an innate quantity of $^{37}Cl_4$-2,3,7,8-TCDD. Except at high concentrations of native 2,3,7,8-TCDD, this contribution is too small to significantly affect the calculated concentration of surrogate $^{37}Cl_4$-2,3,7,8-TCDD. The theoretical correction is calculable on the basis of isotope distribution and amounts to 1.08% of the m/z 257 peak. (This correction should be checked at low resolution by analyzing about 200 pg/ul of unlabelled 2,3,7,8-TCDD.) On this basis, the correction to the area count of the surrogate, is made as follows:

$$A_{263} = A_{263} - 0.0108\ A_{257}$$

Calculate the analytical percent recovery of the surrogate standard.

$$\text{Surrogate Analytical Percent Recovery} = \frac{\text{amount measured* (nanograms)}}{5\ \text{ng}} \times 100$$

* NOTE: The amount measured is equal to the concentration found by equation X multiplied by the weight of soil used for the sample (i.e., $C_{ss} \times W$).

XIII. METHOD PERFORMANCE

The required detection limit for this method is 0.3 ug/kg. For certain samples, this detection limit may not be achievable because of interferences. These samples require cleanup as described in Section XI. This method has been compared with the EPA-IFB GC/MS Method for 2,3,7,8-TCDD and found to be applicable to analyses of soils where 2,3,7,8-TCDD is the only tetrachloro isomer known to be present.

TABLE I

OPERATING CONDITIONS FOR DB-5 GAS CHROMATOGRAPHY COLUMN

COLUMN	DB-5
Length	15 m
I. D.	0.32 mm
Film Thickness	1.0 micron
2,3,7,8-TCDD R. T. (approx.)	5-6 min.
Carrier gas	N_2
Initial Temperature	150°C
Initial Time	1.0 min.
Splitless Time	1.0 min.
Program Rate	20°C/min.
Final Temperature	240°C
Split Flow	20 ml/min.
Septum Purge Flow	0.6 ml/min.
Capillary Head Pressure	8 psi
Transfer Line Temperature	240°C

Instrument	TAGA® or TAGA® 6000E
Ion Source	Townsend/glow discharge CI
CI Reagent Gas	Zero grade air (H_2 and He free)
Reagent Gas Flow	35 ± ml/min.
Source Temperature	200°C
Discharge Current	-1 mA
Q1 Resolution	3 amu at 50% peak height at m/z = 320 (single MS)
Q3 Resolution	3 amu at 50% peak height at m/z = 320 (single MS)
Collision Energy (LAB)	55eV [(OR + GR)/2-R2] or 55eV (OR - R_2)
Collision Gas	Ar
Collision Gas Thickness	400 x 10^{12} molecules/cm^2

019030

Ions Monitored	Q_2	Q_3
	320	257 (native-TCDD)
	322	259 (native-TCDD)
	328	263 (surrogate standard)
	332	268 (internal standard)

XIV. DATA REPORTING

Report all data in units of micrograms per kilogram of wet soil. Use three significant figures at concentrations above 1 ug/kg and 2 significant figures at concentrations below 1 ug/kg. The data package must include the following information:

1. Individual and mean response factor for the three-point calibration of unlabelled 2,3,7,8-TCDD. (Based on High level standard only).

2. Individual and mean response factors for the isotopic surrogate standard (based on high level standard only).

3. The individual ratios of the sum of areas 257 and 259 ions to the 268 ion for 20 replicate measurements of the blank (i.e., sample spiking solution), and the mean Correction Factor based on these ratios.

4. The empirical limit of detection based on the 20 blank measurements.

5. The daily or shift verification of the mean response factors.

6. The percent accuracy i.e., (analytical percent recovery) for the surrogate standard.

7. The result for the method blank.

8. The percent recovery of native TCDD from the spiked sample.

9. The result for the PE sample

10. The result for the field blank.

11. The data filename (to facilitate data retrieval).

12. The sample identification number (as assigned by the field sampling team).

13. Analytical date and time.

14. The area responses for ions 257, 259, 263, and 268.

15. The observed response ratio of ions 257/259 for the sample.

16. The calculated value for native 2,3,7,8-TCDD. (Values above or below 0.3 ug/kg are to be reported only if qualitative identification criteria are met.)

17. If no 2,3,7,8-TCDD was detected, report "not detected" or N.D. and the 0.3 ug/kg required detection limit.

18. The mass chromatograms for all samples and standards. Include both the real-time display data and reduced data showing limits of integration. Include any computer generated response tables.

19. The weight of the original wet sample aliquot.

20. Documentation on the source and history of the native and labelled 2,3,7,8-TCDD standards used.

21. Any other supporting documentation. An example of the required data format follows:

ION	ION	ION	ION	BLANK	NATIVE
ID	257	259	268	RESPONSE	CONC
1					
2					
3					
4					
5					
6					
7					
8					
9					
10					
11					
12					
13					
14					
15					
16					
17					
18					
19					
20					
C.F.					
LOD					

...IVE RF	NATIVE CONC	1	LAB:
...RROGATE RF	SURROGATE CONC	0.3	DATE:
...ON RATIO	I STD CONC	5	CASE NO:
...ITION FACTOR			

...LYSIS DATE	ANALYSIS TIME	ION 257	ION 259	ION 263	ION 268	RATIO 257/259	RF NATIVE	MAT RF % DIFF	RF SURROGATE	RF SURR %DIFF	COMMENTS (25 CHAR MAX)

019034

...L NATIVE RESPONSE FACTOR OUTSIDE LIMITS
...L NATIVE ION RATIO OUTSIDE LIMITS

SURROGATE CONC
I STD CONC
RF NATIVE
RF SURROGATE
ION RATIO AVERAGE
CORRECTION FACTOR

AB	SMO	EPA	ANALYSIS		WET WT	ION	ION	ION	ION	RATIO	SURR	UG/KG
PLE #	SAMPLE #	SAMPLE #	DATE	TIME	GRAMS	257	259	263	268	257/259	ACC	TCDD

SRD AMPLE NO	EPA SAMPLE NO	ANALYSIS DATE	ANALYSIS TIME	NATIVE RATIO	SURROGATE % ACC	TCDD CONC	DL	COMMENTS

L SURROGATE PERCENT ACCURACY OUTSIDE LIMITS
DL HIGH DETECTION LIMIT

Calculations:

* Note: The equivalent concentrations of 2,3,7,8-TCDD (last column) are calculated using Equation VI

$$C_b = \frac{A_b * Q_{is}}{A_{is} * RRF_s * W}$$

Other calculations required are:

1. Equation V: Correction Factor (C.F.) for Blank Contribution

$$C.F. = \frac{\Sigma B}{n} = \_\_\_\_\_$$

2. Equation VII: (Standard Deviation of the Blank Responses)

$$S_b = \frac{(\Sigma C_b^2) - (\Sigma C_b)^2/n}{n-1} \_\_\_\_\_$$

3. Equation VIII: (Limit of Detection based on "Well Known" Blank)

$$LOD = 2 * t * S_b = \_\_\_\_\_$$

ATTACHMENT 3

USEPA CONTRACT LABORATORY PROGRAM STATEMENT OF WORK (SOW) FOR RAPID TURNAROUND DIOXIN ANALYSIS MULTI-MEDIA

ATTACHMENT 3

FINAL

019039

USEPA CONTRACT LABORATORY PROGRAM

STATEMENT OF WORK (SOW)

FOR

RAPID TURNAROUND DIOXIN ANALYSIS

MULTI-MEDIA

NOVEMBER 1986

THIS EXCERPT CONTAINS ONLY EXHIBIT III, 2. SOLID SAMPLES, Pages III-32 to III-71, OF THIS DOCUMENT.

I. SCOPE AND APPLICATION

This method is for use in the rapid determination of 2,3,7,8-Tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) in soil/sediment, dust, wood fiber, vegetation and insulation when 2,3,7,8-TCDD is known to be the principal or only tetrachlorodibenzodioxin isomer present. The method is not specific for the 2,3,7,8-TCDD isomer, unless a capillary column which separates that isomer from the other 21 TCDD isomers is employed. The method is applicable in the concentration range of 0.3-25 ug/kg.

The method employs a tandem quadrupole mass spectrometer (MS/MS) as the final detector. The specificity of detection inherent in such a system significantly reduces the need for sample cleanup. This, in turn, improves productivity and cost-effectiveness relative to other high resolution and low resolution GC/MS analysis techniques. The apparatus and methods described are designed for use in a mobile laboratory, which permits on-site analyses.

The method is intended to be used when analytical results are required rapidly, such as when site cleanup operations are in progress. Since the method is not isomer specific, false positives, including isomers other than 2,3,7,8-TCDD, may occur. But errors in this regard would be on the side of safety. Emphasis in the method is placed on avoiding false negatives, as this is a more critical consideration when public health is to be protected.

This method is restricted to use only by or under the supervision of analysts experienced in the use of gas chromatography/triple quadrupole mass spectrometers and skilled in the interpretation of mass spectra.

Because of the extreme toxicity of this compound, the analyst must prevent exposure to himself, or to others, by materials known or believed to contain 2,3,7,8-TCDD. Section IV of this method contains guidelines and protocols that serve as minimum safe-handling standards in a limited access laboratory.

Analyte	CAS Number
2,3,7,8-TCDD	1746-01-6

II. SUMMARY OF METHOD

Five (5) grams of anhydrous sodium sulfate is placed in a 10 ml serum vial and the vial with cap and septum is weighed. Approximately 5 grams of a soil sample is added and the vial is re-weighed. The sample is spiked with internal and surrogate standards of isotopically labelled 2,3,7,8-TCDD. The sample is mixed by shaking, and extracted with acetonitrile/dichloromethane in the closed vial. An aliquot of the extract is taken and, after separation from acetonitrile, the dichloromethane is used directly for GC/MS/MS analysis. Clean-up should usually not be necessary for soil/sediment samples, but may be necessary for other solid matrices analyzed by this method, therefore, a clean-up procedure is included for those samples which do not meet quality assurance criteria. Concentration of the extract may be done to lower the minimum detectable concentration. Capillary column GC/MS/MS conditions are described which allow for separation of TCDD from the bulk sample matrix and measurement of TCDD in the extract.

Quantification is based on the response of native TCDD relative to the isotopically labelled TCDD internal standard. Performance is assessed based on the results for surrogate standard recoveries, EPA performance evaluation samples, spike recovery tests, and method and field blanks.

III. INTERFERENCES

Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing hardware that lead to discrete artifacts and/or elevated backgrounds at the ions monitored. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory method blanks as described in Section VIII.

The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the sample. 2,3,7,8-TCDD is often associated with other interfering chlorinated compounds which are at concentrations several magnitudes higher than that of 2,3,7,8-TCDD.

The use of a triple quadrupole mass spectrometer as the detector serves to minimize the influence of many of these interferents.

IV. SAFETY

The following safety practices are excerpted directly from EPA Method 613, Section 4 (July 1982 version): See following page.

... a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are identified[8-10]. Benzene and 2,3,7,8-TCDD have been identified as suspected human or mammalian carcinogens.

4.2 Each laboratory must develop a strict safety program for handling of 2,3,7,8-TCDD. The following laboratory practices are recommended:

4.2.1 Contamination of the laboratory will be minimized by conducting all manipulations in a hood.

4.2.2 The effluents of sample splitters for the gas chromatograph and roughing pumps on the GC/MS should pass through either a column of activated charcoal or be bubbled through a trap containing oil or high-boiling alcohols.

4.2.3 Liquid waste should be dissolved in methanol or ethanol and irradiated with ultraviolet light with wavelength greater than 290 nm for several days. (Use F 40 BL lamps or equivalent.) Analyze liquid wastes and dispose of the solutions when 2,3,7,8-TCDD can no longer be detected.

4.3 Dow Chemical U.S.A. has issued the following precautions (revised 11/78) for safe handling of 2,3,7,8-TCDD in the laboratory:

4.3.1 The following statements on safe handling are as complete as possible on the basis of available toxicological information. The precautions for safe handling and use are necessarily general in nature since detailed, specific recommendations can be made only for the particular exposure and circumstances of each individual use. Inquiries about specific operations or uses may be addressed to the Dow Chemical Company. Assistance in evaluating the health hazards of particular plant conditions may be obtained from certain consulting laboratories and from State Departments of Health or of Labor, many of which have an industrial health service. 2,3,7,8-TCDD is extremely toxic to ... been handled for years without injury in analytical and biological laboratories. Techniques used in handling radioactive and infectious materials are applicable to 2,3,7,8-TCDD.

4.3.1.1 Protective Equipment: Throw-away plastic gloves, apron or lab coat, safety glasses and lab hood adequate for radioactive work.

4.3.1.2 Training: Workers must be trained in the proper method of removing of contaminated gloves and clothing without contacting the exterior surfaces.

4.3.1.3 Personal Hygiene: Thorough washing of hands and forearms after each manipulation and before breaks (coffee, lunch, and shift).

4.3.1.4 Confinement: Isolated work area, posted with signs, segregated glassware and tools, plastic-backed absorbent paper on benchtops.

4.3.1.5 Waste: Good technique includes minimizing contaminated waste. Plastic bag liners should be used in waste cans. Janitors must be trained in safe handling of waste.

4.3.1.6 Disposal of Wastes: 2,3,7,8-TCDD decomposes above 800 °C. Low-level waste such as the absorbent paper, tissues, animal remains and plastic gloves may be burned in a good incinerator. Gross quantities (milligrams) should be packaged securely and disposed through commercial or governmental channels which are capable of handling high-level radioactive wastes or extremely toxic wastes. Liquids should be allowed to evaporate in a good hood and in a disposable container. Residues may then be handled as above.

4.3.1.7 Decontamination: Personal—any mild soap with plenty of scrubbing action. Glassware, Tools, and Surfaces—Chlorothene NU Solvent (Trademark of the Dow Chemical Company) is the least toxic solvent shown to be effective. Satisfactory cleaning may be accomplished by rinsing with Chlorothene, then washing with any detergent and water. Dish water may be disposed to the sewer. It is prudent to minimize solvent wastes because they may require special disposal through commercial sources which are expensive.

4.3.1.8 Laundry: Clothing known to be contaminated should be disposed with the precautions described under "Disposal of Wastes." Lab coats or other clothing worn in 2,3,7,8-TCDD should be collected in plastic bags. Persons who convey the bags and launder the clothing should be advised of the hazard and trained in proper handling. The clothing may be put into a washer without contact if the launderer knows the problem. The washer should be run through a cycle before being used again for other clothing.

4.3.1.9 Wipe Tests: A useful method of determining cleanliness of work surfaces and tool is to wipe the surface with a piece of filter paper. Extraction and analysis by gas chromatography can achieve a limit of sensitivity of 0.1 μg per wipe. Less than 1 μg 2,3,7,8-TCDD per sample indicates acceptable cleanliness; anything higher warrants further cleaning. More than 10 μg on a wipe sample indicates an acute hazard and requires prompt cleaning before further use of the equipment or work space and indicates further that unacceptable work practices have been employed in the past.

4.3.1.10 Inhalation. Any procedure that may produce airborne contamination must be done with good ventilation. Gross losses to a ventilation system must not be allowed. Handling of the dilute solutions normally used in analytical and animal work presents no inhalation hazards except in case of an accident.

4.3.1.11 Accidents. Remove contaminated clothing immediately, taking precautions not to contaminate skin or other articles. Wash exposed skin vigorously and repeatedly until medical attention is obtained.

V. APPARATUS AND MATERIALS

All glassware is initially cleaned with aqueous detergent and then rinsed with tap water, deionized water, acetone, toluene and methylene chloride. Other cleaning procedures may be used as long as acceptable method blanks are obtained.

Electronic balance, capable of weighing at least 50 g, with an accuracy of at least ± 0.05 g.

Shaker, vortex-type or equivalent

Centrifuge, 4000 rpm, capable of handling 25 mm diameter vials

Centrifuge tubes

10 ml serum vials; with teflon faced septa and aluminum caps (Chrompak 10204 and 10213 or equivalent)

1 ml serum vials; with teflon faced septa and aluminum caps (Chrompak 10201 and 10211 or equivalent)

Crimper for 10 ml serum vial (Chrompak 10233 or equivalent)

Crimper for 1 ml serum vial (Chrompak 10231 or equivalent)

Disposable teflon 0.45 micron filters (Millipore SLHV025 HB, or equivalent)

5 ml disposable Glaspak syringes (Sargent Welch S-79401-B or equivalent)

18 gauge disposable syringe needle (Sargent Welch S-79402-G or equivalent)

Disposable pipets, 5 3/4 inches x 7 mm o.d.

Glass wool, silanized

Nitrogen blowdown apparatus

Gas chromatograph - an analytical system with all required accessories including syringes and analytical columns. The injection port must be designed for capillary columns and splitless injection.

Triple quadrupole mass spectrometer with GC transfer line and glow discharge ion source (TAGA® 6000, SCIEX©, or equivalent)

Compressed Gases: Zero Grade Air (from distillation, not water hydrolysis)
Ultra High Purity Nitrogen
Ultra High Purity Argon

Column: 15 m long, wide bore fused silica capillary (eg. 0.32 mm I.D.)
DB-5 1.0 micron film thickness.

VI. REAGENTS

Stock Standard Solutions

Stock standard solutions correspond to three toluene solutions containin unlabelled 2,3,7,8-TCDD at varying concentrations, and $^{13}C_{12}$-2,3,7,8-TCDD (internal standard, CASRN 80494-19-5) at a constant concentration. These solutions also contain $^{37}Cl_4$-2,3,7,8-TCDD (surrogate compound, CASRN 85508-50-5) at varying concentrations. These stock solutions are to be used in preparing the calibration standard solutions, and are to be obtained from the Quality Assurance Division, USEPA, Environmental Monitoring Systems Laboratory (EMSL-LV), Las Vegas, Nevada. If not available from EMSL-LV, stock standard solutions may be prepared from commercially available standards. However, the accuracy of these solutions must be checked against EPA supplied standard solutions.

The three stock solutions will have the following concentrations of unlabelled, internal and surrogate standards.

Stock Solution #1 (CC1)

Unlabeled 2,3,7,8-TCDD - 0.2 ng/ul
$^{13}C_{12}$-2,3,7,8-TCDD - 1.0 ng/ul
$^{37}Cl_4$-2,3,7,8-TCDD - 0.06 ng/ul

Stock Solution #2 (CC2)

Unlabeled 2,3,7,8-TCDD - 1.0 ng/ul
$^{13}C_{12}$-2,3,7,8-TCDD - 1.0 ng/ul
$^{37}Cl_4$-2,3,7,8-TCDD - 0.12 ng/ul

Stock Solution #3 (CC3)

Unlabeled 2,3,7,8-TCDD - 5.0 ng/ul
$^{13}C_{12}$-2,3,7,8-TCDD - 1.0 ng/ul
$^{37}Cl_4$-2,3,7,8-TCDD - 0.2 ng/ul

NOTE: Store stock solutions in 1 ml amber mini-vials under refrigeration.

Calibration Standard Solutions

Calibration standard solutions are prepared to simulate the conditions of sample analysis as nearly as possible. Three calibration standard solutions are prepared from the stock standard solutions so as to contain constant amounts of internal standard (5 ug/kg equivalent) with variable amounts of unlabeled standard (1,5, and 25 ug/kg equivalent) and surrogate standard (0.3, 0.6, and 1.0 ug/kg equivalent). The equivalent concentrations are based on the use of 5-gram samples, extraction with 5 ml of 2:1 acetonitrile: dichloromethane, and a final extract volume of approximately 1.66 ml dichloromethane after removal of acetonitrile, as called for in the procedure.

Low Level

Add 750 ul of stock solution #1 to a 5 ml volumetric flask and bring to volume with dichloromethane. Mix well. This solution contains an equivalent concentration of 1 ug/kg of 2,3,7,8-TCDD, 5 ug/kg of $^{13}C_{12}$-2,3,7,8-TCDD, and 0.3 ug/kg of $^{37}Cl_4$-2,3,7,8-TCDD.

Medium Level

Add 750 ul of stock solution #2 to a 5 ml volumetric flask and bring to volume with dichloromethane. Mix well. This solution contains an equivalent concentration of 5 ug/kg of 2,3,7,8-TCDD, 5 ug/kg of $^{13}C_{12}$-2,3,7,8-TCDD, and 0.6 ug/kg of $^{37}Cl_4$-2,3,7,8-TCDD.

High Level

Add 750 ul of stock solution #3 to a 5 ml volumetric flask and bring to volume with dichloromethane. Mix well. This solution contains an equivalent concentration of 25 ug/kg of 2,3,7,8-TCDD, 5 ug/kg of $^{13}C_{12}$-2,3,7,8-TCDD, and 1.0 ug/kg of $^{37}Cl_4$-2,3,7,8-TCDD.

NOTE 1: Although the surrogate, $^{37}Cl_4$-2,3,7,8-TCDD, is present in all three level calibration solutions, only the high level solution is used for calculating the relative response factor for the surrogate.

NOTE 2: All calibration standard solutions must be stored in an isolated refrigerator and protected from light. Check these standard solutions frequently for signs of evaporation.

Sample Spiking Solution

The sample spiking solution is also to be obtained from the Quality Assurance Division, U. S. EPA Environmental Monitoring Systems Laboratory (EMSL-LV), Las Vegas, Nevada. The spiking solution will have the following concentrations of internal and surrogate standards.

$^{13}C_{12}$-2,3,7,8-TCDD - 0.5 ng/ul
$^{37}Cl_4$-2,3,7,8-TCDD - 0.1 ng/ul

When 50 ul of this solution is spiked in 5 g of soil, the resulting concentrations in the soil are 5 ug/kg and 1 ug/kg of internal and surrogate standard, respectively.

It is recommended that approximately 2.5-5 ml of the spiking solution be transferred to a 5 ml serum vial and sealed with a septum and cap prior to each day's work for use in spiking samples that day.

NOTE: It is very important that no evaporation of sample spiking solution be allowed to occur, since the accuracy of results are directly dependent on the addition of a known amount of internal standard.

Fortified Field Blank Spiking Solution

The fortified field blank spiking solution is also to be obtained from the Quality Assurance Division, U. S. EPA, Environmental Monitoring Systems Laboratory (EMSL-LV), Las Vegas, Nevada. The spiking solution will have the following concentrations of unlabelled, internal, and surrogate standards:

2,3,7,8-TCDD - 0.1 ng/ul
$^{13}C_{12}$-2,3,7,8-TCDD - 0.5 ng/ul
$^{37}Cl_4$-2,3,7,8-TCDD - 0.1 ng/ul

When 50 ul of this solution is spiked in 5 grams of soil, the resulting concentrations in the soil are 5 ug/kg of internal standard and 1 ug/kg each of unlabelled and surrogate standard.

NOTE: It is very important that no evaporation of field blank spiking solution be allowed to occur, since the accuracy of results are directly dependent on the addition of a known amount of internal standard.

Solvent

All solvents should be pesticide grade or equivalent. The following solvents will be needed:

Acetonitrile
Dichloromethane
Cyclohexane
Toluene
Benzene
Methanol

Silica Gel

Type 60, 70-230 mesh. Soxhlet extracted with dichloromethane for 24 hours, then activated for 24 hours at 130°C.

Acid Alumina

AG 4, 100-200 mesh. soxhlet extracted with dichloromethane for 24 hours, then activated for 24 hours at 190°C.

Carbopack C, 80/100 mesh or equivalent

Celite 545, not acid washed, or equivalent

Sodium Sulfate

(ACS) granular, anhydrous.

VII. CALIBRATION AND LIMIT OF DETECTION DETERMINATIONS

Calibration must be done using the internal standard technique. In this case, the internal standard is an isotope of the compound-of-interest, and

therefore, the technique is also referred to as isotope-dilution-mass spectrometry. The three calibration standard solutions described in section VI are required.

Inject 1-2 ul of each of the calibration standard solutions and acquire selected reaction monitoring data for the following parent- daughter ions:

m/z = 320 257
m/z = 322 259
m/z = 328 263
m/z = 332 268

For simplicity in subsequent sections, we will refer only to the daughter ions, since quantitation is based on daughter ion response.

Relative response factors for unlabelled 2,3,7,8-TCDD vs the internal standard for triplicate determinations of each of the three calibration standard solutions are calculated.

Equation I: Relative Response Factor (RRFs) for 2,3,7,8-TCDD

$$RRFs = (A_s C_{is})/(A_{is} C_s)$$

where A_s = the sum of the area responses for the ions, m/z 257 and 259, corresponding to the unlabelled standard, 2,3,7,8-TCDD.

A_{is} = the area response of the ion m/z 268, corresponding to the internal standard, $^{13}C_{12}$-2,3,7,8-TCDD.

C_s = the concentration of the unlabelled standard, 2,3,7,8-TCDD

C_{is} = the concentration of the internal standard, $^{13}C_{12}$-2,3,7,8-TCDD.

In the case of the unlabelled 2,3,7,8-TCDD each of the calibration standard solutions must be analyzed in triplicate, and the variation of the RRF values for each compound at each concentration level must not exceed 10% RSD. If the three mean RRF values for each compound do not differ by more than $\pm$ 10%, the RRF can be considered to be independent of analyte quantity for the calibration concentration range, and the mean of the three mean RRFs shall be used for concentration calculations. The overall mean is termed a calibration factor.

Similarly, relative response factors for the surrogate standard vs the internal standard for the triplicate determinations of the high level calibration solution are also calculated.

Equation II: Relative Response Factor (RRF_{ss}) for $^{37}Cl_4$-2,3,7,8-TCDD

$$RRF_{ss} = (A_{ss} C_{is})/(A_{is} C_{ss})$$

where A_{ss} = the area response of the daughter ion, m/z 263, corresponding to the surrogate standard, $^{37}Cl_4$-2,3,7,8-TCDD.*

* Subtract 0.0108 of any 257 response from the 263 response to correct for contributions of 2,3,7,8-TCDD to the 263 response.

A_{is} = the area response of the ion m/z 268, corresponding to the internal standard, $^{13}C_{12}$-2,3,7,8-TCDD.

C_{ss} = the concentration of the surrogate standard, $^{37}Cl_4$-2,3,7,8-TCDD.

and C_{is} = the concentration of the internal standard, $^{13}C_{12}$-2,3,7,8-TCDD.

In the case of the surrogate standard, $^{37}Cl_4$-2,3,7,8-TCDD, the variation of the three RRF values for the high level calibration solution should not exceed 10% RSD. If this is the case, the mean of the three RRFs shall be used for concentration calculations. The overall mean is termed a calibration factor.

The calibration factor for the unlabelled 2,3,7,8-TCDD must be verified on each work shift of 12 hours or less by the analysis of a low level calibration standard. If the RRF for the low level calibration differs from the calibration factor by more than 10%, the entire calibration must be repeated and a new calibration factor determined. The overall mean relative response factor must be used in all calculations. This verification is only required for the unlabelled standards. There is no need to check the surrogate calibration factor unless the surrogate recoveries appear biased or consistently fall outside the 60-140% control limits.

The theoretical ratio of the m/z 257 to 259 ions for native 2,3,7,8-TCDD is 1.02. However, in practice this ratio will differ from the theoretical due to the very low resolution used in both analyzing quadrupoles for this type of analysis. The ratio must therefore, be determined empirically as follows:

Equation III: (Ratio of native TCDD daughter ions)

$$\text{Ratio} = A_{257}/A_{259}$$

where A_{257} = Area response for ion m/z 257

A_{259} = Area response for ion m/z 259

The mean of the ratios calculated for each of the nine calibration solutions is used for comparison purposes for qualitative identification of 2,3,7,8-TCDD. An acceptable ion ratio range is determined by taking $\pm$10% of the mean ratios for the nine calibration analyses.

It has been found that the sample spiking solution also gives responses for the 257 and 259 daughter ions corresponding to 2,3,7,8-TCDD. These contributions must be subtracted out for each sample. In order to determine this correction factor, add 150 ul of the sample spiking solution to a 5 ml volumetric flask and bring to volume with dichloromethane. Twenty 1-2 ul injections of this solution must be made and the ratio of the area responses for the sum of the m/z 257 and 259 ions vs the m/z 268 ion must be calculated. Twenty separate ratios must be determined.

Equation IV: Blank Response (B) of Sample Spiking Solution

$$B = A_b/A_{is}$$

where A_b = the sum of the area responses for the ions, m/z 257 and 259, obtained with the spiking solution

and A_{is} = The area response of the ion m/z 268, corresponding to the internal standard $^{13}C_{12}$-2,3,7,8-TCDD present in the spiking solution.

The correction factor for the blank contribution to sample response is then calculated as the mean of the 20 blank responses.

Equation V: Correction Factor (C.F.) for Blank Contribution

$$C.F. = \frac{\sum B}{n}$$

where B = The sum of the individual blank responses determined by Equation IV.

n = Number of replicate measurements of the blank response (20 are required for initial determination).

Limit Of Detection

The empirical limit of detection will be calculated based on the variability of the blank responses. The blank responses correspond to those obtained from repeat injections of the (diluted) sample spiking solution. Each blank response must be converted to an equivalent concentration of 2,3,7,8-TCDD.

Equation VI: (Conversion of Blank Response to An Equivalent Concentration of 2,3,7,8-TCDD)

$$C_b = \frac{A_b \times Q_{is}}{A_{is} \times RRF_s \times W} = \frac{25 \times A_b}{5 \times A_{is} \times RRF_s}$$

where C_b = equivalent concentration of 2,3,7,8-TCDD in blank (spiking solution) (in units of ug/kg or ppb)

A_b = the sum of the area responses of the ions m/z 257 and 259 for the blank

A_{is} = the area response of the ion m/z 268, corresponding to the internal standard

RRF_s = The relative response factor previously determined for 2,3,7,8-TCDD (Equation I)

Q_{is} = 25 nanograms (the weight of internal standard added to each sample)

W = 5 grams (the weight of wet soil used for each sample)

The standard deviation of the blank responses (in concentration units must then be calculated.

Equation VII: (Standard Deviation of The Blank Responses)

$$S_b = \sqrt{\frac{(\Sigma C_b^2) - (\Sigma C_b)^2/n}{n-1}}$$

where S_b = standard deviation of the blank responses (in units of ug/

C_b = blank response in concentration units (calculated using Equation VI)

n = number of replicate blank results used (20 are required)

Finally, the limit of detection must be calculated from the standard deviation of the blank.

Equation VIII: (Limit of Detection Based on "Well-Known" Blank)*

$$LOD = 2\ t\ S_b$$

where LOD = Limit of Detection

t = the 10% point of the t statistic for a double-sided table with n-1 degrees of freedom (where n is equal to the nu of blank results used). NOTE: The LOD must be calculat based on at least 20 replicate blank (i.e. spiking solu analyses. For n = 20, t = 1.72.

The limit of detection calculated from equation VIII should be less t the required limit of detection of 0.3 ug/kg.

VIII. QUALITY CONTROL REQUIREMENTS

The following quality control (Q.C.) requirements are listed in the order that they must be run. Requirements 1 and 2 are to be run initially before any other samples. Requirement 3 is to be included with each batch real samples that is run in one 12-hour time period or on each shift. The requirements 4 and 9 are to be met for each set of samples analyzed. Items 5, 6, and 7 are to be met for each set of samples if submitted by the sampl team. Note: Requirements 4-8 are considered automatic rerun criteria and therefore are part of the principal sample analysis and are not billable.

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* Reference - Currie, Lloyd A. "Limits for Qualitative Detection and Quantitative Determination" Anal, Chem., 40, 3, 586-593, 1968

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1. An initial calibration must be performed using calibration standard solutions with varied (1,5, and 25 ug/kg equivalent) native TCDD and 5 ug/kg equivalent internal standard. Calibration for the surrogate standard will be based only on the high level standard (1 ug/kg equivalent). The criteria given in Section VII must be met or the calibration must be repeated. All samples associated with an unacceptable initial calibration must be reanalyzed

2. Initially, 20 replicate determinations of the spiking solution must be run and a correction factor calculated. Twenty separate ratios must be determined (Equation IV) and used in calculating the mean correction factor (Equation V).

3. A 1-point check verification using the 1 ug/kg equivalent native TCDI and 5 ug/kg equivalent internal standard must be run once every 12 hours or on every shift, whichever is more frequent. If the RRF values from this calibration check differ by more than $\pm$ 10% from the previously determined mean relative response factor (RRFs), the 3-point calibration must be repeated. All samples associated with an unacceptable 1-point calibration check must be reanalyzed. The calibration check for the surrogate is not necessary unless the surrogate recoveries appear biased and/or consistently fall outside the 60-140% control limits.

4. A laboratory "reagent blank" must be run along with each batch of 24 or fewer samples. A reagent blank is performed by executing all of the specified extraction steps, except for the introduction of a 5 gram sample. The reagent blank is also dosed with the internal standard and surrogate standard. Results for the reagent blank must be calculated the same way as samples. This includes correction for the spiking solution contribution as indicated in Equation IX. A positive response $\geq$ 0.3 ug/kg of native TCDD must be followed by reinjection. If still positive, re-extraction and reanalysis of all related positive samples must be done.

5. "Field blanks" may be provided to monitor for possible cross-contamination of samples in the lab. The "field blank" will consist of uncontaminated soil (background soil taken off-site). A positive response $\geq$ 0.3 ug/kg native TCDD must be followed by reinjection. If still positive, all positive samples associated with the field blanks must be re-extracted and reanalyzed.

6. One sample may be provided by EPA, and must be spiked with native 2,3,7,8-TCDD at a level of 1 ug/kg for each set of 24 or fewer samples. The Field Blank Spiking Solution (Section VI) should be used to spike the designated sample. The recovery must be 0.6 to 1.4 ug/kg or the analysis stopped and all related samples must be re-extracted and reanalyzed.

7. The laboratory may be given performance evaluation samples by EPA to run with each batch of samples. The results from these performance evaluation samples will be evaluated by EPA. If a result is not within the acceptance criteria set by EPA, all samples in the batch associated with that PE sample must be re-extracted and reanalyzed.

8. Each sample must be dosed with 50 ul of the sample spiking solution containing internal standard (equivalent to 5.0 ug/kg) and surrogate standard (equivalent to 1.0 ug/kg). The surrogate recovery must be 0.6 to 1.4 ug/kg or the sample must be re-extracted and reanalyzed.

9. Qualitative requirements a-e must be met in order to confirm the presence of native 2,3,7,8-TCDD; qualitative requirements d and e must be met in order to confirm the absence of native 2,3,7,8-TCDD.

a. The retention time must equal (within 3 seconds) the retention time for the internal standard.

b. The 257/259 ratio must be within the range ± 10% of the value of the mean ratio determined in Section VII, (Equation III).

c. The ion responses at 257 and 259 must be present and maximize together. The signal to mean noise ratio must be 2.5 to 1 or better for both daughter ions. (Determine the noise level by measuring the random peak to valley signal present on either side [within 20 scans] of the 2,3,7,8-TCDD retention window. The 2,3,7,8-TCDD signal must be at least 2.5 times larger than this.)

d. For those samples giving non-detect results, the result must be less than the 0.3 ug/kg required limit of detection. Otherwise the analysis must be stopped and interferences identified and corrected until the 0.3 ug/kg required limit of detection is met.

e. For each sample, the internal standard must be present with at least a 10 to 1 signal to noise ratio based on the m/z 268 ion response.

IX. SAMPLE COLLECTION, PRESERVATION AND HANDLING

The procedures for sample collection, shipping and handling will be specified by the EPA Regional Office responsible for the monitoring exercise. The sampling team will be provided with an 8 ounce glass jar, and 30-300 grams of soil will be collected. When received in the laboratory, the sample should be thoroughly mixed in the jar for a minimum of 3 minutes, using a stainless steel spatula. The spatula should be used to break up large clumps of soil while mixing to achieve a homogeneous sample.

A 5 gram aliquot sample must be taken and placed in a pre-weighed 10 ml serum vial containing approximately 5 grams of anhydrous sodium sulfate together with a Teflon-faced septum and cap. (The entire vial, Na_2SO_4, septum and cap is pre-weighed and labelled). The 5 gram aliquot sample should be representative of the entire sample. Thus, large stones or other particles which are uncharacteristic of the sample, should not be included in the aliquot.

Samples may be stored under ambient conditions as long as temperature extremes (below freezing or above 90°F) are avoided. Samples must be protected from light to avoid photodecomposition.

All samples must be extracted and completely analyzed within 24 hours. Extracts must be held for 7 days following EDS and unused sample portions for 30 days following EDS, prior to disposal. Sample extracts and unused sample portions must be submitted within 7 days of written request by the Project Officer or SMO.

X. SAMPLE EXTRACTION

CAUTION: Although the sample and standards are sealed throughout the extraction procedure, there is always the possibility of leakage and breakage (especially during the sample spiking and centrifuging steps). The analyst should, therefore, be fully protected by wearing plastic gloves and laboratory jacket (a face protector is optional). See Section IV for details on specific safety requirements.

1. Prepare extraction solvent by mixing two volumes acetonitrile with one volume dichloromethane. Mix solvents thoroughly.

2. Add approximately 5 g. of sample to the sample vial containing 5 g. anhydrous sodium sulfate and determine the net weight of sample (to 3 significant figures).

3. Add 50 ul of the sample spiking solution (containing both internal and surrogate standards). The solution will contain 0.5 ng/ul of internal standard and 0.1 ng/ul of surrogate standard. Add the 50 ul solution directly to the soil, spreading it over several sites on the surface of the soil.

4. Attempt to mix the soil and sodium sulfate by shaking. (Extremely wet samples may not mix well, but DO NOT open the vial to stir the contents.) Additional anhydrous sodium sulfate should be added if needed.

5. Pierce the septum with a disposable needle and leave the needle in place to vent the contents while the extraction solvent is introduced.

6. Add 5 ml of the 2:1 acetonitrile: dichloromethane extraction solvent using a 5 ml syringe and disposable needle. Retain the syringe for solvent additions only.

NOTE: Additional extraction solvent can be added if the analyst judges this necessary to achieve efficient extraction on a particular sample.

7. Remove the syringe and both needles (they should be treated as though contaminated). Dispose of both needles.

8. Shake the vial vigorously on a vortex mixer for 2 minutes.

9. Centrifuge the vial and contents at 4000 rpm for 2 minutes. Remove carefully so as not to disturb the sediment.

10. Insert a needle through the septum so that it just breaks the surface of the septum inside the vial. Using a clean disposable syringe and needle, withdraw approximately 1 ml of the extract; NOTE: The other needle through the septum serves to equilibrate the pressure upon withdrawal of the extract.

11. Invert the syringe and withdraw the plunger to remove the extract from the needle. Dispose of the needle (it is contaminated).

12. Place a 0.45 micron disposable Teflon filter on the syringe and inject the extract into a clean 10 ml serum vial containing 9 ml distilled water. Dispose of the syringe and the filter.

13. Using a Teflon lined septum and an aluminum cap, cover and crimp the vial containing the water-extract mixture.

14. Manually shake the vial vigorously for about one minute.

15. Centrifuge the vial to separate the dichloromethane phase from the water/acetonitrile phase. The dichloromethane phase will appear as a small bubble at the bottom of the vial.

16. Prepare a miniature drying tube as follows:

a. Plug the tip of a disposable pipet with a small amount of silanized glass wool.

b. Add approximately 1/2 cm anhydrous sodium sulfate.

17. With a disposable syringe and needle, remove the dichloromethane phase from the vial (step 15) as completely as possible.

18. Transfer the dichloromethane phase through the drying tube into a clean 1 ml serum vial.

19. Rinse the drying tube with one-half ml dichloromethane, and collect in the same 1 ml serum vial.

20. Under a stream of nitrogen, evaporate the solvent gently until the volume of solution remaining in the serum vial is 0.05-0.1 ml.

21. Seal the 1 ml serum vial with a Teflon lined septum and cap. Label the vial appropriately.

XI. CLEANUP

The need for cleanup is indicated when a particular extract does not meet the QC criteria for the coelution of all four monitored ions, surrogate recovery, the ratio A_{257}/A_{259}, or the signal to noise ratio for ion 268. It has been noted that dust samples often contain matrix interferences which coelute with native TCDD and should be processed using both cleanup procedures. Two cleanup procedures are given below.

A. Modified Option A Cleanup

1. Plug the tip of a disposable pipet with a small amount of silanized glass wool.

2. Place approximately a 1 cm layer of silica gel over the glass wool.

3. Place approximately a one-half cm layer of anhydrous sodium sulfate over the silica gel.

4. Plug the tip of a second disposable pipet with a small amount of silanized glass wool.

5. Place approximately 0.5 cm acid alumina over the silanized glass wool.

6. Place approximately 0.5 cm anhydrous sodium sulfate over the alumina.

7. Arrange the two columns so that the silica gel column will elute onto the alumina column, and the alumina column drippings will be collected in a vial.

8. Rinse the two columns with 0.5 ml cyclohexane and discard the eluate.

9. Open the vial containing the extract and add 1 ml cyclohexane to the extract.

10. Under a stream of nitrogen, carefully evaporate the dichloromethane from the extract vial (the volume of the remaining solution should be just under 1 ml).

11. Transfer the entire contents of the extract vial onto the silica column, arranged as specified in step 7.

12. When the solution just reaches the surface of the sodium sulfate layer in the silica gel column, add 0.5 ml cyclohexane.

13. Repeat step 12 a second time. Allow the solution to drip completely after the second addition of cyclohexane.

14. Discard the silica gel column.

15. Rinse the alumina column with an additional 1 ml cyclohexane. Discard the accumulated eluates in the vial beneath the column.

16. Place a clean 1 ml serum vial under the alumina column.

17. Elute the alumina column with three successive portions of 0.5 ml each of 15% by volume dichloromethane in cyclohexane, collecting the eluate in the clean vial.

18. With gentle heating and under a stream of nitrogen, evaporate the solvent until the volume in the vial is 0.05-0.1 ml.

19. Seal the serum vial with a teflon lined septum and cap. Label the vial appropriately. NOTE: If it is a priori known that the second step of cleanup is required, evaporate the sample in stage 18 to just below 1 ml and immediately proceed with a second cleanup as described below.

B. Option D Cleanup

All samples indicating the presence of other TCDD isomers or which contain compounds co-eluting must be cleaned up using Option D.

1. In advance, prepare a mixture of 3.6 g Carbopack C with 16.4 g Celite 545. Activate the mixture at 130°C for 6 hours.

2. Plug the tip of a disposable pipet with a small amount of silanized glass wool.

3. Place 2 cm layer of the carbopack-Celite mixture over the glass wool plug, using suction to pack the column.

4. Rinse the column sequentially with 2 ml toluene, 1 ml dichloromethane-methanol-benzene (75:20:5 by volume), 1 ml cyclohexane-dichloromethane 1:1 by volume), and finally 2 ml cyclohexane. Collect the eluate in a vial and discard the eluate.

5. Dilute the extract which has been cleaned up by the Modified Option A procedure to 1 ml with cyclohexane.

6. Maintaining a discard vial under the column, introduce the extract onto the column.

7. After the solvent has drained, rinse the column successively with 2 ml cyclohexane, 1 ml cyclohexane-dichloromethane mixture (1:1 by volume) and 1 ml dichloromethane-methanol-benzene mixture (75:20:5 by volume).

8. Allow the column to drain completely and discard the accumulated eluates.

9. Place a clean serum vial under the column.

10. Elute the dioxin from the charcoal with 2 ml toluene.

11. With gentle heating and under a stream of nitrogen, concentrate the extract to a volume of 0.05-0.1 ml.

12. Seal the serum vial with a Teflon lined septum and cap. Label appropriately

XII. GC/MS/MS ANALYSIS

1. Table 1 summarizes the 15 m DB-5 gas chromatographic capillary column and operating conditions. The 15 m DB-5 column has been used for chromatography which is not isomer specific (no valley is observed between the 1,2,3,4-TCDD and 2,3,7,8-TCDD isomers).

2. Standards and samples must be analyzed under identical MS/MS conditions. Selected Reaction Monitoring (SRM) scans are used, using a scan time to give at least five points per chromatographic peak. Recommended MS/MS conditions are given in Table 2.

3. Verify the Calibration of the system as described in Section VII. The volume of calibration standard injected should be approximately the same as all sample injection volumes. The requirements described in Section VIII, Parts 9a, b, c and e must be met for all calibration standards.

4. Inject a 1 to 2 ul aliquot of the sample extract.

5. The presence/absence of TCDD is qualitatively confirmed if the criteria of Section VIII, Part 9, are achieved.

6. For quantitation, measure the area response of the m/z 257 and 259 peaks for 2,3,7,8-TCDD; the m/z 268 peak for $^{13}C_{12}$-2,3,7,8-TCDD, and the m/z 263 peak for $^{37}Cl_4$-2,3,7,8-TCDD. Calculate the concentrations of native and surrogate standards using the following equations:

Equation IX: (Calculation of concentration of native 2,3,7,8-TCDD)

$$C_s = \frac{((A_s/A_{is}) - C.F.)\ (Q_{is})}{RRFs \times W}$$

where C_s = The concentration of native 2,3,7,8-TCDD in ug/kg

A_s = the sum of the area responses for the ions, m/z 257 and 259

A_{is} = the area response for the ion m/z 268

C.F. = correction factor for spiking solution (blank) previously determined (Equation V)

Q_{is} = qantity (in nanograms) of $^{13}C_{12}$-2,3,7,8-TCDD added to the sample before extraction

RRF_s = Overall mean relative response factor for 2,3,7,8-TCDD calculated previously (Equation I) for the initial calibration.

W = weight (in grams) of wet soil or sediment sample.

In evaluating the results, a distinction must be made between quantitative measurement and qualitative identification of 2,3,7,8-TCDD. The following steps must be followed in the treatment of all sample results:

1. Calculate the concentration of native 2,3,7,8-TCDD using equation IX.

2. Determine if all of the qualitative identification criteria are met.

3. If all qualitative identification criteria are met, report the concentration found by equation IX, regardless of concentration.

4. If the qualitative identification criteria are not met, and the concentration calculated by equation IX is less than the required limit of detection of 0.3 ug/kg, report the concentration as less than 0.3 ug/kg (i.e. <0.3 ug/kg).

5. If the qualitative identification criteria are not met, and the concentration calculated by equation IX is greater than the required limit of detection of 0.3 ug/kg, the extract must be reinjected. If the qualitative identification criteria are still not met and the result is still greater than 0.3 ug/kg, the extract must be cleaned up or the sample reanalyzed until a satisfactory result is obtained. (i.e. positive result or negative result below 0.3 ug/kg).

NOTE: In reporting results for sample analysis, a comparison is made with the required limit of detection. The limit of detection based on the blank (Equation VIII) might also be used, but interferences may be present and introduce false positives in some cases. However, as explained in Section VII, the empirical limit of detection based on the blank must be less than the required limit of detection of 0.3 ug/kg.

Equation X: (Calculation of concentration of surrogate standard, $^{37}Cl_4$-2,3,7,8-TCDD)

$$C_{ss} = \frac{A_{ss} \times Q_{is}}{A_{is} \times RRF_{ss} \times W}$$

where C_{ss} = the concentration of surrogate standard $^{37}Cl_4$-2,3,7,8-TCDD in ug/kg.

A_{ss} = the area response for the ion m/z 263*

A_{is} = the area response for the ion m/z 268

Q_{is} = quantity (in nanograms) of $^{13}C_{12}$-2,3,7,8-TCDD added to the sample before extraction.

RRF_{ss} = Overall mean relative response factor for $^{37}Cl_4$-2,3,7,8-TCDD calculated previously (Equation II) from the high level initial calibration standard.

W = Weight (in grams) of wet soil or sediment sample.

* Subtract 0.0108 of any 257 response from the 263 response to correct for contributions of any 2,3,7,8-TCDD to the 263 response.

Native 2,3,7,8-TCDD contains an innate quantity of $^{37}Cl_4$-2,3,7,8-TCDD. Except at high concentrations of native 2,3,7,8-TCDD, this contribution is too small to significantly affect the calculated concentration of surrogate $^{37}Cl_4$-2,3,7,8-TCDD. The theoretical correction is calculable on the basis of isotope distribution and amounts to 1.08% of the m/z 257 peak. (This correction should be checked at low resolution by analyzing about 200 pg/ul of unlabelled 2,3,7,8-TCDD.) On this basis, the correction to the area count of the surrogate, is made as follows:

$$A_{263} = A_{263} - 0.0108\ A_{257}$$

Calculate the analytical percent recovery of the surrogate standard.

$$\text{Surrogate Analytical Percent Recovery} = \frac{\text{amount measured* (nanograms)}}{5\ \text{ng}} \times 100$$

* NOTE: The amount measured is equal to the concentration found by equation X multiplied by the weight of soil used for the sample (i.e., $C_{ss} \times W$).

XIII. METHOD PERFORMANCE

The required detection limit for this method is 0.3 ug/kg. For certain samples, this detection limit may not be achievable because of interferences. These samples require cleanup as described in Section XI. This method has been compared with the EPA-IFB GC/MS Method for 2,3,7,8-TCDD and found to be applicable to analyses of soils where 2,3,7,8-TCDD is the only tetrachloro isomer known to be present.

TABLE I

OPERATING CONDITIONS FOR DB-5 GAS CHROMATOGRAPHY COLUMN

COLUMN	DB-5
Length	15 m
I. D.	0.32 mm
Film Thickness	1.0 micron
2,3,7,8-TCDD R. T. (approx.)	5-6 min.
Carrier gas	N_2
Initial Temperature	150°C
Initial Time	1.0 min.
Splitless Time	1.0 min.
Program Rate	20°C/min.
Final Temperature	240°C
Split Flow	20 ml/min.
Septum Purge Flow	0.6 ml/min.
Capillary Head Pressure	8 psi
Transfer Line Temperature	240°C

TABLE 2

MS/MS OPERATING CONDITIONS

Instrument	TAGA® or TAGA® 6000E
Ion Source	Townsend/glow discharge CI
CI Reagent Gas	Zero grade air (H_2 and He free)
Reagent Gas Flow	35 ± ml/min.
Source Temperature	200°C
Discharge Current	-1 mA
Q1 Resolution	3 amu at 50% peak height at m/z = 320 (single MS
Q3 Resolution	3 amu at 50% peak height at m/z = 320 (single MS
Collision Energy (LAB)	55eV [(OR + GR)/2-R2] or 55eV (OR - R_2)
Collision Gas	Ar
Collision Gas Thickness	400 x 10^{12} molecules/cm^2

Ions Monitored:	Q_2	Q_3
	320	257 (native-TCDD)
	322	259 (native-TCDD)
	328	263 (surrogate standard)
	332	268 (internal standard)

XIV. DATA REPORTING

Report all data in units of micrograms per kilogram of wet soil. Use three significant figures at concentrations above 1 ug/kg and 2 significant figures at concentrations below 1 ug/kg. See Exhibit II for specific data reporting requirements.

I. Scope and Application

This method is for use in the rapid determination of 2,3,7,8-Tetrachlorodibenzo-p-dioxin in soil and sediment at concentrations of 1 ug/Kg to to 25 ug/Kg in 10-g aliquots of wet soil/sediment. This method may also be used for other solid matrices such as dust, wood fiber, vegetation and insulation samples. The minimum measurable concentration is estimated to be 0.3 ug/Kg, but is dependent on interfering compounds present in the sample matrix. The method includes a rapid preparation procedure, which is estimated to permit the processing of 24 samples for GC/MS analysis in 10 hours. Thus, the method is particularly applicable when rapid analyses are required, such as in site cleanup operations.

The method is intended to be used in those cases where 2,3,7,8-TCDD is known to be the only isomer of concern. Therefore, there is no requirement that isomer specificity be demonstrated. This approach is a conservative one when applied to cleanup operations, since false negatives are of more concern than false positives. An optional procedure is included for use when the demonstration of isomer specificity is judged necessary.

The final measurement process utilizes low resolution mass spectrometry. This measurement is restricted to use only by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. (Note-High resolution mass spectrometry may also be used, but is not necessary).

Because of the extreme toxicity of this compound, the analyst must prevent exposure to himself, or to others, by materials known or believed to contain 2,3,7,8-TCDD. Section IV of this method contains guidelines and protocols that serve as minimum safe-handling standards in a limited access laboratory.

Analyte	CAS Number
2,3,7,8-TCDD	1746-01-6

II. Summary of Method

A 10-gram sample of soil is spiked with internal and surrogate standards of isotopically labeled 2,3,7,8-TCDD. The wet sample is mixed with 20 grams of anhydrous sodium sulfate prior to extraction with acetone/hexane using a jar extraction technique. The method provides cleanup procedures to aid in the elimination of interferences that may be encountered. The extract is concentrated to a volume of 50 uL. Capillary column GC/MS conditions are described which allow for the separation and measurement of 2,3,7,8-TCDD in the extract. Quantitation is based on the response of native TCDD relative to the isotopically labeled TCDD internal standard. Performance is assessed based on extensive quality assurance requirements (Section VIII). These include a requirement for accuracy of surrogate measurement on each sample.

III. Interferences

Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated backgrounds at the ions monitored. All of these materials must be routinely demonstrated to be free from interference under the conditions of the analysis by running laboratory method blanks as described in Section VIII.

The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

Silica gel, alumina, and carbon column cleanup procedures have been included to remove interferences present in samples (Section XI).

IV. Safety

The following safety practices are excerpted directly from EPA Method 613 Section 4 (July 1982 version): See following page.

In addition to the EPA Method 613 concerns, the analyst should note that finely divided dry soils contaminated with TCDD are particularly hazardous because of the potential for inhalation and ingestion of fine particulates containing TCDD. It is recommended that such samples be processed in a confined environment, such as a hood or glove box. Lab personnel handling these types of samples should also wear masks fitted with charcoal adsorbent media to prevent inhalation of dust.

V. Apparatus and Materials

All glassware is initially cleaned with aqueous detergent and then rinsed with tap water, deionized water, acetone, toluene, and methylene chloride. Other cleaning procedures may be used as long as acceptable method blanks are obtained.

Grab sample bottle - glass, pint volume, fitted with screw caps lined with Teflon. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The container must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

Clearly label all samples as "FLAMMABLE SOLID" and ship according to DOT requirements.

not been precisely defined; however,

each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are identified[8-10]. Benzene and 2,3,7,8-TCDD have been identified as suspected human or mammalian carcinogens.

4.2 Each laboratory must develop a strict safety program for handling of 2,3,7,8-TCDD. The following laboratory practices are recommended:

4.2.1 Contamination of the laboratory will be minimized by conducting all manipulations in a hood.

4.2.2 The effluents of sample splitters for the gas chromatograph and roughing pumps on the GC/MS should pass through either a column of activated charcoal or be bubbled through a trap containing oil or high-boiling alcohols.

4.2.3 Liquid waste should be dissolved in methanol or ethanol and irradiated with ultraviolet light with wavelength greater than 290 nm for several days. [Use F 40 BL lamps or equivalent.] Analyze liquid wastes and dispose of the solutions when 2,3,7,8-TCDD can no longer be detected.

4.3 Dow Chemical U.S.A. has issued the following precautions (revised 11/78) for safe handling of 2,3,7,8-TCDD in the laboratory:

4.3.1 The following statements on safe handling are as complete as possible on the basis of available toxicological information. The precautions for safe handling and use are necessarily general in nature since detailed, specific recommendations can be made only for the particular exposure and circumstances of each individual use. Inquiries about specific operations or uses may be addressed to the Dow Chemical Company. Assistance in evaluating the health hazards of particular plant conditions may be obtained from certain consulting laboratories and from State Departments of Health or of Labor, many of which have an industrial health service. 2,3,7,8-TCDD is extremely toxic to laboratory animals. However, it has been handled for years without injury in analytical and biological laboratories. Techniques used in handling radioactive and infectious materials are applicable to 2,3,7,8-TCDD.

4.3.1.1 Protective Equipment: Throw-away plastic gloves, apron or lab coat, safety glasses and lab hood adequate for radioactive work.

4.3.1.2 Training: Workers must be trained in the proper method of removing of contaminated gloves and clothing without contacting the exterior surfaces.

4.3.1.3 Personal Hygiene: Thorough washing of hands and forearms after each manipulation and before breaks (coffee, lunch, and shift).

4.3.1.4 Confinement: Isolated work area, posted with signs, segregated glassware and tools, plastic-backed absorbent paper on benchtops.

4.3.1.5 Waste: Good technique includes minimizing contaminated waste. Plastic bag liners should be used in waste cans. Janitors must be trained in safe handling of waste.

4.3.1.6 Disposal of Wastes: 2,3,7,8-TCDD decomposes above 800 °C. Low-level waste such as the absorbent paper, tissues, animal remains and plastic gloves may be burned in a good incinerator. Gross quantities (milligrams) should be packaged securely and disposed through commercial or governmental channels which are capable of handling high-level radioactive wastes or extremely toxic wastes. Liquids should be allowed to evaporate in a good hood and in a disposable container. Residues may then be handled as above.

4.3.1.7 Decontamination: Personal—any mild soap with plenty of scrubbing action. Glassware, Tools, and Surfaces—Chlorothene NU Solvent (Trademark of the Dow Chemical Company) is the least toxic solvent shown to be effective. Satisfactory cleaning may be accomplished by rinsing with Chlorothene, then washing with any detergent and water. Dish water may be disposed to the sewer. It is prudent to minimize solvent wastes because they may require special disposal through commercial sources which are expensive.

4.3.1.8 Laundry: Clothing known to be contaminated should be disposed with the precautions described under "Disposal of Wastes." Lab coats or other clothing worn in 2,3,7,8-TCDD work area may be laundered. Clothing should be collected in plastic bags. Persons who convey the bags and launder the clothing should be advised of the hazard and trained in proper handling. The clothing may be put into a washer without contact if the launderer knows the problem. The washer should be run through a cycle before being used again for other clothing.

4.3.1.9 Wipe Tests: A useful method of determining cleanliness of work surfaces and tool is to wipe the surface with a piece of filter paper. Extraction and analysis by gas chromatography can achieve a limit of sensitivity of 0.1 μg per wipe. Less than 1 μg 2,3,7,8-TCDD per sample indicates acceptable cleanliness; anything higher warrants further cleaning. More than 10 μg on a wipe sample indicates an acute hazard and requires prompt cleaning before further use of the equipment or work space and indicates further that unacceptable work practices have been employed in the past.

4.3.1.10 Inhalation: Any procedure that may produce airborne contamination must be done with good ventilation. Gross losses to a ventilation system must not be allowed. Handling of the dilute solutions normally used in analytical and animal work presents no inhalation hazards except in case of an accident.

4.3.1.11 Accidents: Remove contaminated clothing immediately, taking precautions not to contaminate skin or other articles. Wash exposed skin vigorously and repeatedly until medical attention is obtained.

Concentrator tube, Kuderna-Danish - 10-mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

Evaporative flask, Kuderna-Danish - 500-mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

Snyder column, Kuderna-Danish - three-ball macro (Kontes K-503000-0121 or equivalent).

Minivials - 1.0 mL vials; cone shaped inside to enable removing very small samples; heavy wall borosilicate glass; with Teflon® faced rubber septa and screw caps.

Gas chromatograph - An analytical system complete with all required accessories including syringes, analytical columns, and gases. The injection port must be designed for capillary columns. Either split, splitless, or on-column injection techniques may be employed.

Nitrogen blowdown apparatus, N-Evap® Analytical Evaporator Model 111 (or equivalent).

Disposable pipet, 5 3/4 inches X 7.0 mm o.d.

Balance - Analytical, capable of accurately weighing 0.001 g.

Columns

30 m long X 0.32 mm ID fused silica capillary DB-5, with 0.25u film thickness.

Other columns can be used as long as the quality control requirements are met, including isomer specificity if necessary.

Mass Spectrometer - Either low resolution mass spectrometers (LRMS) or high resolution mass spectrometers (HRMS) may be used. The mass spectrometer must be equipped with a 70 volt (nominal) ion source and be capable of acquiring ion abundance data in real time Selected Ion Monitoring (SIM) for groups of six or more ions. The electron impact ionization mode must be used.

GC/MS interface - Any gas chromatograph to mass spectrometer interface can be used that achieves the requirements of Section VIII. Glass or glass-lined materials are recommended. Glass surfaces can be deactivated by silanizing with dichlorodimethylsilane. To achieve maximum sensitivity, the exit end of the capillary column should be placed in the ion source. A short piece of fused silica capillary can be used as the interface to overcome problems associated with straightening the exit end of glass capillary columns.

The SIM data acquired during the chromatographic program can be acquired under computer control or as real time analog output. If computer control is used, there must be software available to plot the SIM data and report peak height or area for any ion between specified time or scan number limits.

VI. Reagents

Concentration Calibration Solutions

Three toluene solutions containing unlabeled 2,3,7,8-TCDD at varying concentrations and $^{13}C_{12}$-2,3,7,8-TCDD (the internal standard, CASRN 80494-19-5) at a constant concentration. These solutions also contain $^{37}Cl_4$-2,3,7,8-TCDD(the surrogate compound, CASRN 85508-50-5) at varying concentrations. Concentration calibration solutions are to be obtained from the Quality Assurance Division, USEPA Environmental Monitoring SYSTEMS Laboratory (EMSL-LV), Las Vegas, Nevada. However, if not available from EMSL-LV, standards may be obtained from commercial sources, and solutions may be prepared in the contractor laboratory. Traceability of standards must be verified against EPA-supplied standard solutions.

Each of solutions #1-#3 contains $^{13}C_{12}$-2,3,7,8-TCDD at a concentration of 1 ng/uL, which is intended to simulate the concentration in an extract for a sample spiked with $^{13}C_{12}$-2,3,7,8-TCDD at a concentration of 5 ug/kg.

Solutions #1-#3 contain unlabeled 2,3,7,8-TCDD at concentrations of 0.2, 1.0, and 5.0 ng/uL, respectively, which are intended to simulate concentrations in extracts of samples containing 1, 5, and 25 ug/kg.

Solutions #1-#3 contain $^{37}Cl_4$-2,3,7,8-TCDD at concentrations of 0.06, 0.12, and 0.2 ng/uL, respectively, which are intended to simulate concentrations in extracts of samples containing 0.3, 0.6, and 1.0 ug/kg.

NOTE 1 - the simulated concentrations assume no losses of 2,3,7,8-TCDD or its isomers during sample preparation. This is not the case, but since the internal standard calibration is based on ratios of responses rather than absolute responses, no error is introduced into calibration as a result of the assumption.

NOTE 2 - Store calibration solutions in 1 ml amber mini-vials under refrigeration.

GC/MS interface - Any gas chromatograph to mass spectrometer interface can be used that achieves the requirements of Section VIII. Glass or glass-lined materials are recommended. Glass surfaces can be deactivated by silanizing with dichlorodimethylsilane. To achieve maximum sensitivity, the exit end of the capillary column should be placed in the ion source. A short piece of fused silica capillary can be used as the interface to overcome problems associated with straightening the exit end of glass capillary columns.

The SIM data acquired during the chromatographic program can be acquired under computer control or as real time analog output. If computer control is used, there must be software available to plot the SIM data and report peak height or area for any ion between specified time or scan number limits.

VI. Reagents

Concentration Calibration Solutions

Three toluene solutions containing unlabeled 2,3,7,8-TCDD at varying concentrations and $^{13}C_{12}$-2,3,7,8-TCDD (the internal standard, CASRN 80494-19-5) at a constant concentration. These solutions also contain $^{37}Cl_4$-2,3,7,8-TCDD(the surrogate compound, CASRN 85508-50-5) at varying concentrations. Concentration calibration solutions are to be obtained from the Quality Assurance Division, USEPA Environmental Monitoring SYSTEMS Laboratory (EMSL-LV), Las Vegas, Nevada. However, if not available from EMSL-LV, standards may be obtained from commercial sources, and solutions may be prepared in the contractor laboratory. Traceability of standards must be verified against EPA-supplied standard solutions.

Each of solutions #1-#3 contains $^{13}C_{12}$-2,3,7,8-TCDD at a concentration of 1 ng/uL, which is intended to simulate the concentration in an extract for a sample spiked with $^{13}C_{12}$-2,3,7,8-TCDD at a concentration of 5 ug/kg.

Solutions #1-#3 contain unlabeled 2,3,7,8-TCDD at concentrations of 0.2, 1.0, and 5.0 ng/uL, respectively, which are intended to simulate concentrations in extracts of samples containing 1, 5, and 25 ug/kg.

Solutions #1-#3 contain $^{37}Cl_4$-2,3,7,8-TCDD at concentrations of 0.06, 0.12, and 0.2 ng/uL, respectively, which are intended to simulate concentrations in extracts of samples containing 0.3, 0.6, and 1.0 ug/kg.

NOTE 1 - the simulated concentrations assume no losses of 2,3,7,8-TCDD or its isomers during sample preparation. This is not the case, but since the internal standard calibration is based on ratios of responses rather than absolute responses, no error is introduced into calibration as a result of the assumption.

NOTE 2 - Store calibration solutions in 1 ml amber mini-vials under refrigeration.

Sulfuric acid - impregnated silica gel (40% w/w) - add two parts concentrated sulfuric acid to three parts silica gel in a screw capped bottle and mix until lump free.

Carbopak C, 80/100 mesh, or equivalent.

Celite 545, not acid washed, or equivalent.

Carbopak C/Celite mixture - A mixture by weight of 18% Carbopak C on Celite is prepared. This is mixed throughly on a vortex mixture to break up large lumps. Check visually to assure that the mixture is uniform.

VII. Calibration

Calibration must be done using the internal standard technique. By injecting calibration standards, establish ion response factors for 2,3,7,8-TCDD vs. the internal standard ($^{13}C_{12}$ 2,3,7,8-TCDD), and for the surrogate standard ($^{37}Cl_4$ 2,3,7,8-TCDD) vs. the internal standard ($^{13}C_{12}$ 2,3,7,8-TCDD). Standard solutions equivalent to 1, 5, and 25 ug/Kg are required for routine work.

Using injections of 1 to 3 uL, tabulate peak height or area response of 2,3,7,8-TCDD vs. internal standard and $^{37}Cl_4$ 2,3,7,8-TCDD vs. internal standard and calculate relative response factors (RRF) for both native TCDD and surrogate standard TCDD using Equations 1 and 2.

Equation 1 (RRF for native 2,3,7,8-TCDD)

$$RRF = (AsCis)/(AisCs)$$

where: As = SIM response for 2,3,7,8-TCDD (m/e 320 + 322)
Ais = SIM response for $^{13}C_{12}$ 2,3,7,8-TCDD internal standard (m/e 332 + 334)

Cs = Concentration of 2,3,7,8-TCDD (pg/uL)

Equation 2 (RRF for surrogate standard, $^{37}Cl_4$ 2,3,7,8-TCDD)

$$RRF = (AssCis)/(AisCss)$$

where: Ass = SIM response for $^{37}Cl_4$ 2,3,7,8-TCDD (m/e 328)*
Ais = SIM response for $^{13}C_{12}$ 2,3,7,8-TCDD internal standard (m/e 332 + 334)
Cis = Concentration of the internal standard (pg/uL)
Css = Concentration of the surrogate standard $^{37}Cl_4$ 2,3,7,8-TCDD (pg/uL)

*When using $^{37}Cl_4$-TCDD, correct the 328 response by subtracting 0.009 of the 322 response.

Cis = Concentration of the internal standard (pg/uL)

Each of the calibration standard solutions must be analyzed in triplicate, and the variation of the RRF values for each compound at each concentration level must not exceed 10% RSD. If the three mean RRF values for each compound do not differ by more than +/-10% RSD, the RRF can be considered to be independent of analyte quantity for the calibration concentration range, and the mean of the three mean RRFs shall be used for the concentration calculations. The overall mean is termed a calibration factor.

The calibration factor must be verified on each work shift of 12-hours or less by the analysis of the 1 ug/kg standard. If the RRF for the standard differs from the calibration factor by more than 10%, the entire calibration must be repeated and a new calibration factor determined. The overall mean RRF determined during the initial calibration must be used for both native 2,3,7,8-TCDD and surrogate calculations.

VIII. Quality Control Requirements

1. Each sample must be dosed with a known quantity of internal standard (equivalent to 5.0 ug/Kg) and surrogate standard (equivalent to 1.0 ug/Kg).

The action limits for surrogate standard results will be ± 40% of the true value. Samples showing surrogate standard results outside of these limits must be reextracted and reanalyzed.

2. A laboratory "reagent blank" must be analyzed along with each set of 24 or fewer samples. A reagent blank is performed by executing all of the specified extraction and cleanup steps, except for the introduction of a 10-gram sample. The reagent blank is also dosed with the internal standard and surrogate standard. The reagent blank result must be less than 0.1 ug/Kg. If a result of 0.1 ug/kg or greater is obtained, all positive samples in the set must be reextracted and reanalyzed.

3. An EPA performance evaluation sample may be given to the lab by EPA and must be analyzed along with each set of 24 or fewer samples. The result must meet accuracy requirements specified by EPA. If the requirements are not met, all samples in the set must be reextracted and reanalyzed.

4. Qualitative identification requirements. The following requirements must be met in order to confirm the presence of native 2,3,7,8-TCDD.

a.) The 320/322 ratio must be within the range of 0.67 to 0.90.

b.) Ions 320, 322, and 257, must all be present and maximize together. The signal to mean noise ratio must be 2.5 to 1 or better for all 3 ions. (Determine the noise level by measuring the random peak to valley signal present on eigher side [within 20 scans] of the 2,3,7,8-TCDD retention window. The 2,3,7,8-TCDD signal must be at least 2.5 times larger than this.)

c.) The retention time must equal (within 3 seconds) the retention time for the isotopically labeled 2,3,7,8-TCDD.

d.) (Optional, depending on project needs) Isomer specificity must be demonstrated initially and verified once per 12-hour work shift. The verification consists of injecting a mixture containing TCDD isomers which elute close to 2,3,7,8-TCDD. This mixture will be provided by EPA. It contains seven TCDD isomers (2378, 1478, 1234, 1237, 1238, 1278, 1267) including those isomers which are known to be the most difficult to separate on SP2330/SP2340 columns and similar columns containing cyanoalkyl type liquid phases. The column performance solution (Section VI) must also contain both isotopically labeled 2,3,7,8-TCDD standards. The solution must be analyzed using the same chromatographic conditions and mass spectrometric conditions as is used for other samples and standards. The 2,3,7,8-TCDD must be separated from interferring isomers, with no more than a 50% valley relative to the 2,3,7,8-TCDD peak.

Draw a baseline for the isomer cluster representing 1478, 2378, 1237, 1238, and 1234-TCDD. Measure the distance x from the baseline to the valley following the 2,3,7,8-TCDD peak (use the valley preceding the 2,3,7,8-TCDD peak if it is higher). Measure the distance y from the baseline to the apex of the 2,3,7,8-TCDD peak. Distance x over distance y times 100 is the percent valley which must not exceed 25. An example is given in Figure 1.

5. EPA may designate one sample to be spiked with native 2,3,7,8-TCDD at a level of 1.0 PPB for each set of 24 or fewer samples. EPA will designate the sample to be dosed.

6. Detection Limit: A detection limit must be calculated for every sample not giving a positive result meeting all criteria for qualitative identification. The detection limit is used to estimate a concentration above which 2,3,7,8-TCDD is probably not present. Two cases may arise, each requiring a different procedure to calculate the detection limit.

The background noise level must be determined in both cases, and is defined as the mean area (or height) of the background signal in adjacent areas of the SICP for either the m/z 320 or m/z 322 ion, depending on which one is chosen. Peak height is used rather than peak area because of the difficulty of integrating random peak areas for background-noise.

a.) For samples in which no unlabeled 2,3,7,8-TCDD was detected, calculate the detection limit as the concentration required to produce a signal with area (or peak height) of 2.5 times the background signal area (or peak height). The background area is determined by integrating ion abundances for either m/z 320 or 322 in the appropriate region of the SICP, multiplying that area by 2.5, and relating the product area to an estimated concentration that would produce that product area.

Use equation (3) and multiply result by 2.5.

i.e. Concentration, ng/g = 2.5 x (As)(Is)/(Ais)(RRF)(W)
where the terms are as defined in equation (3).

b.) For samples having interference in the responses for both m/z 320 and 322, or when a ratio not meeting the quality control criteria prevented identification of 2,3,7,8-TCDD, the detection limit is calculated using equation 3.

i.e. Concentration, ng/g = (As)(Is)/(Ais)(RRF)(W)

The detection limit in this case is then the estimated concentration of 2,3,7,8-TCDD, assuming that interference or ratio criteria problems were not present. It is unlikely that 2,3,7,8-TCDD could be present at a concentration greater than this estimated detection limit.

7. For each sample, the internal standard must be present with at least a 10 to 1 signal to noise ratio for both mass 332 and mass 334. Also, the internal standard 332/334 ratio must be within the range of 0.67 to 0.90.

8. Where appropriate, "field blanks" will be provided to monitor for possible cross contamination of samples in the laboratory and field, and to monitor sampling containers and supplies. The "field blank" will consist of uncontaminated soil (background soil taken off-site). A positive response greater than 0.1 ug/kg of native 2,3,7,8-TCDD must be followed by cleanup and reinjection. If still positive, then re-extract and analyze the field blank, re-extract and re-analyze all positive samples in the set.

IX. Sample Collection, Preservation, and Handling

Sample collection personnel will, to the extent possible, homogenize samples in the field prior to the filling of sample containers. This should minimize or eliminate the necessity for sample homogenization in the lab. The analyst should make a judgment, based on the appearance of the sample, regarding the necessity for additional mixing. If the sample is clearly inhomogeneous, the entire contents should be transferred to a glass or stainless steel pan for mixing with a stainless steel spoon or spatula prior to removal of the 10-gram aliquot.

Samples may be stored under ambient conditions as long as temperature extremes (below freezing or above 90°F) are avoided. Samples must be protected from light to avoid photodecomposition.

All samples must be extracted and completely analyzed within 24 hours. Extracts must be held for 7 days following EDS and unused sample portions for 30 days following EDS, prior to disposal. Sample extracts and unused sample portions must be submitted within 7 days of written request by the Project Officer or SMO.

X. Sample Extraction (Jar Method)

CAUTION: When using this method to analyze for 2,3,7,8-TCDD, all of the following operations should be performed in a limited access laboratory with the analyst wearing full protective covering for all exposed skin surfaces. All handling of sample containers should be in a fume hood. See Section IV for details on specific safety requirements.

All glassware and equipment should be cleaned and assembled prior to the weighing of the samples. A system to identify or label each sample throughout all sections of the procedure is recommended.

Preliminary Treatment

1. Transfer a 10-gram (10 to 12 grams weighed to 3 significant figures) aliquot of sample directly into the extraction jar. Each sample should be scooped with an individual stainless steel spatula to avoid cross contamination.

2. Crush the larger pieces of dirt with the spatula. Leaving the spatula in the jar, cover the mouth of the jar with a teflon-lined lid.

3. Using a 250 ul syringe, add 100 ul of spiking standard solution (containing both internal and surrogate standards). This will result in the addition of 50 ng of internal standard and 10 ng of surrogate standard. Add the 100 ul solution chosen directly to the soil, spreading it over several sites on the surface of the soil. Make certain that the standard has absorbed into the soil before continuing the procedure.

4. Excessively wet samples should be centrifuged and moisture decanted, prior to weighing. If the soil sample is moist, add 20 grams of purified anhydrous sodium sulfate to the sample after the spiking solution has dried in the sample. (If the soil sample is relatively dry, no sodium sulfate is required prior to extraction.) Mix thoroughly using a stainless steel spoon or spatula. Allow the mixture to stand for five minutes then continue with the procedure.

Extraction

1. Add 50 ml of 10% acetone/hexane solvent solution to each jar. Allow the solvent to wash down over the spatula. Remove the spatula from the jar. Add the magnetic stir bar and cap the jar tightly.

2. Place the samples on the stirring plates. Adjust the speed of the stir bar to obtain a moderate mixing of the soil sample and solvent. Stir all samples in the set for a minimum of 30 minutes, based on when the last sample of the set has begun mixing. NOTE: Other mixing/stirring devices are acceptable.

Filtering and Kuderna-Danish Concentration

1. Assemple the Kuderna-Danish flasks with receiving tubes in a rack, Add 2-3 teflon boiling chips to each receiving tube. Place a glass funnel containing a #4 Whatman filter paper in each flask. Place 2-5 g of sodium sulfate in each funnel.

2. Remove the jars from the stirrer. Remove each of the caps and rinse the inner surface with hexane so that the solvent washes back into the sample container. Remove the magnetic stir bar and rinse with hexane so that the solvent washes back into the jar.

3. Carefully decant the extract through the funnel into the Kuderna-Danish flask. Rinse the sample with a small volume of hexane. Decant the rinse into the funnel. Rinse the funnel and paper with hexane and remove both after rinsing.

4. Add 1-2 ml of isooctane to the extract in the K-D receiver.

5. Place a Snyder-tube on the K-D flask, then place the K-D assembly on a steam bath.

6. Concentrate the extract to a volume of 1-2 ml.

7. Disconnect the K-D flask from the K-D receiver tube and rinse the tip of the tube with a small volume of hexane. Note: Complete K-D condensation of all sample extracts before transfering them to columns.

XI. Cleanup Procedures

The following cleanup procedure based on column chromatographic adsorption using silica gel, alumina, and activated carbon is recommended for all samples. The internal standard isotope dilution technique corrects for losses during cleanup.

However, before employing the cleanup procedure on any samples, a series of standards should be processed through the procedure in order to verify that internal standard recovery is adequate and that accurate results are obtained for both surrogate and unlabeled 2,3,7,8-TCDD standards.

Column #1 (Silica Gel Column) 1. Optimum results for the sample elution are obtained with single mold glass columns, 40 cm long, 0.9 cm I.D., containing a top reservoir of 50 ml capacity and a 7 cm long stopcock tip. Each column, fitted with a teflon stopcock, is cleaned and solvent rinsed prior to packing.

2. Place a small wad of solvent-activated glass wool in each column and rinse with hexane. Allow the solvent to evaporate.

3. Place 1.0 g of silica gel in each column followed by 4.0 g of 40% w/w sulfuric acid activated silica gel and 0.5 - 1.0 g of anhydrous sodium sulfate.

4. Fill each column reservoir with 30-40 ml of hexane as an initial rinse and wetting agent. Close each stopcock to keep adsorbents wet and activated until clean-up has begun.

Column #2 (Alumina Column) 1. Single mold glass columns, 0.9 cm I.D. and 15 cm long, having a top 50 ml reservoir and a 7 cm long stopcock tip are used for column #2. Each column, containing a teflon stopcock is cleaned and solvent rinsed prior to packing.

2. Place a small wad of solvent rinsed glass wool in each column and rinse with hexane. Allow the solvent to evaporate before proceeding.

3. Place 4.0 g of alumina followed by 0.5-1.0 g of anhydrous sodium sulfate in each column.

4. Place in each reservoir 30-40 ml of hexane for an initial rinse. Close each stopcock to keep the alumina wet and activated while packing other columns.

Column #3 (Activated Carbon Column) 1. Disposable pasteur pipets, 5 3/4" long are used for column #3. Note: These columns can be prepared a day before use.

2. Pack a small wad of solvent rinsed glass wool in each pipet.

3. Add 0.1 - 0.5 g of carbopack, the length of which should be 2 cm from the top of the glass wool plug. (Prepare 18% Carbopak C on Celite 545 by thoroughly mixing 3.6 grams of Carbopak C (80/100 mesh) and 16.4 grams of Celite 545 in a 40 ml vial. Activate at 130°C for six hours. Store in a desiccator.)

Note: Prior to sample elution, a small long-stem glass funnel can be connected to each column #3 pipet with a teflon tube to direct sample/solvent flow and to act as a reservoir.

Column Elution Procedure

Packing of the columns should be done in less than 1-1 1/2 hours prior to sample elution. Adsorbent materials in columns will remain relatively inert (i.e. unreactive) for that time period if the solvent, hexane, has been added immediately after packing. Note, however, that the silica gel columns are more reactive and they should be prepared last. Special attention should be paid to removing bubbles from the solvent soaked absorbent. Columns are efficiently handled on two tiered multi-clamp racks.

1. Drain the hexane rinse from the columns until an adsorbent layer is barely saturated with hexane (application of a low pressure of nitrogen gas will speed the draining of solvent).

2. Align Column #1 over Column #2 to assure collection of sample elute.

3. Using a pasteur pipet, place the sample from the K.D. receiver on Column #1. Rinse the K-D receiver with 4-1/2 ml portions of hexane and place on the column.

4. Add 40 ml of hexane to the receiver of Column #1 and allow the solvent to elute into Column #2.

5. After the hexane has drained into Column #2, remove Column #1.

6. Before the elution of sample is complete from Column #1 to Column #2, rinse Column #3 with 1 ml of toluene and allow to drain. Then rinse Column #3 with 1 ml of 75:20:5 solution of methylene chloride/methanol/benzene. Allow to drain.

7. After Column #2 has drained, place Column #3 under Column #2 and fill the reservoir in Column #2 with 24 ml of 20% methylene chloride in hexane.

8. Remove Column #2 after all the solvent has eluted to Column #3. Rinse Column #3 with 1 ml of a 75:20:5 methylene chloride/methanol/benzene solution.

9. Place a 2 ml Wheaton GC vial under Column #3 after the 75:20:5 rinse is completed.

10. Place 2 ml of toluene on Column #3 and collect in a Wheaton vial. This final elution can be concentrated to a final volume of 50 - 100 ul using a nitrogen evaporation unit.

XII. GC/MS Analysis

1. Immediately before analysis by GC/MS, adjust the sample extract volume to approximately 25 ul.

2. Table I gives guidelines for operating conditions using a DB-5 capillary column. Other columns and/or conditions may be used as long as isomer specificity is demonstrated.

3. Analyze standards and samples with the mass spectrometer operating in the selected ion monitoring (SIM) mode using a scan time to give at least five points per peak. For LRMS, use ions at m/e 320, 322, and 257 for 2,3,7,8-TCDD, m/e 328 for 334 for $^{37}C_4$-2,3,7,8-TCDD, and ions at m/e 332 and $^{37}C_{12}$-2,3,7,8-TCDD. For HRMS, use ions at m/e 319.8965 and 321.8936 for 2 3,7,8-TCDD, ion at m/e 327.8847 for ^{37}Cl-2,3,7,8-TCDD, and ion at m/e 331.9367 for ^{13}C-2,3,7,8-TCDD.

TABLE I

Recommended GC Capillary Conditions

Column	(30 M) DB-5
2,3,7,8-TCDD R. T.	14 Min.
Helium Linear Velocity	1 ml/min.
Initial Temperature	75°C
Initial Time	1.0 min.
Splitless Time	2.0 min.
Program Rate	25° C/min.
Final Temperature	200°C*
Final Hold Time	15 min.
Split Flow	15 ml/min.
Septum Purge Flow	15 ml/min.
Capillary Head Pressure	12 psi

* or 195°C and second ramp at 2°C/min. to 215°C

4. Check the calibration every 12 hours as described in Section VII. The volume of calibration standard injected should be approximately the same as sample injection volumes. The requirements described in Section VIII, Parts 4a, b, c, and 7 must be met for all calibration standards.

5. Inject a 1 to 3 uL aliquot of the sample extract.

6. The presence/absence of 2,3,7,8-TCDD is qualitatively confirmed if the criteria of Section VIII, Parts 4 and 7, are achieved.

7. For quantitation, measure the response of the m/e 320 and 322 peaks for 2,3,7,8-TCDD, the m/e 332 and 334 peaks for $^{13}C_{12}$-2,3,7,8-TCDD, and the 328 peak for $^{37}Cl_4$-2,3,7,8-TCDD. A correction must be made for contribution to m/e 328 by any native TCDD which may be present. To do this, subtract 0.009 of the 322 response from the 328 response. Calculate the concentration of native 2,3,7,8-TCDD using the relative response factor (RRF) and Equation 3. If native TCDD is not present, calculate the detection limit as described in Section VIII, Part 6.

Equation 3 (Calculation of concentration of native 2,3,7,8-TCDD)

Concentration, ng/g = (As)(Is)/(Ais)(RRF)(W)

where: As = SIM response for 2,3,7,8-TCDD ion at m/e 320 + 322
Ais = SIM response for the internal standard ion at m/e 332 + 334
Is = Amount of internal standard added to each sample (ng)
W = Weight of soil in grams

Equation 4 (Calculation of amount of surrogate standard $^{37}Cl_4$ 2,3,7,8-TCDD)

Amount in ng = (Ass)(Is)/(Ais)(RRF)

where: Ass = SIM response for surrogate $^{37}Cl_4$ 2,3,7,8-TCDD ion at m/e 328*
Ais = SIM response for the internal standard ion at m/e 322 + 334
Is = Amount of internal standard added to each sample (ng)

*When using $^{37}Cl_4$-TCDD, subtract 0.009 of any 322 response.

8. Co-eluting impurities are suspected if all criteria except the isotope ratio criteria are achieved. If broad background interference restricts the sensitivity of the GC/MS analysis, the analyst must employ additional cleanup procedures and reanalyze by GC/MS.

9. Calculation of Percent Accuracy of surrogate standard.

% Accuracy = (amount measured in ng/10 ng)(100)

XIII. Method Performance

The required detection limit for this method is 0.3 ug/kg (ng/g). However, for certain samples this detection limit may not be achievable because of interferences. On other relatively clean samples, the estimated detection limit may be quite lower.

XIV. Data Reporting

Report all data in units of micrograms per kilogram (parts per billion) of wet soil. Use three significant figures for values at or above 1.0 ug/kg and two significant figures for values below 1.0 ug/kg. Report percent moisture of the soil if requested. See Exhibit II for specific data reporting requirements.

XV. Sample Reruns

Sample analyses must be repeated if any of the following conditions apply:

1. A detection limit of 0.3 ug/kg could not be achieved. Concentrate extract to 15 uL and reanalyze. If the detection limit is not achieved, re-extract and reanalyze a second aliquot.

2. The percent accuracy for surrogate standard was outside of acceptance limits. Re-extract and reanalyze sample aliquot.

3. The reagent blank contained TCDD at a concentration greater than 0.1 ug/kg. Re-extract and reanalyze the reagent blank all positive samples associated with the reagent blank.

4. The internal standard 332/334 ratio was outside the 0.67-0.90 control limits. Reanalyze the sample extract. Re-extract and reanalyze a sample aliquot if the ratio is still outside the limits.

5. The internal standard was not present with at least 10/1 signal to noise ratio at mass 332 and 334. Concentrate sample extract further and reanalyze. If still not present at required level, re-extract and reanalyze a sample aliquot.

TABLE I

Recommended GC Capillary Conditions

Column	A (Silar 10C)	B (SP2340)
2,3,7,8-TCDD R.T.	34.5 min	22 min
Helium Linear Velocity	30 cm/sec	0.7 ml/min at 60°C
Initial Temperature	100°C	60°C
Initial Time	3.0 min	3 min
Splitless Time		1.0 min
Program Rate	20°C/min	25°C/min
Final Temperature	180°C*	250°C
Final Hold Time	15 min	15 min
Split Flow		30 ml/min
Septum Purge Flow		5 ml/min
Capillary Head Pressure		30 psi

*then 2°/min to 250°C

ATTACHMENT 4

REGIONAL TECHNICAL ASSISTANCE FOR PREPARING QUALITY ASSURANCE PROJECT AND LABORATORY PLANS

ATTACHMENT 4

Draft

019081

Regional Technical Assistance for Preparing Quality Assurance Project and Laboratory Plans

ROQA-005/85
(Revised Jan, 1986)

by

Steven R. Lemons

Office of Quality Assurance
Environmental Services Division
U.S. Environmental Protection Agency, Region VI

January 1, 1985

I. Who must prepare a Quality Assurance Project Plan (QAPjP)

The U.S. EPA Quality Assurance (QA) program embraces many functions including: establishing QA policy and guidelines for development of program and project operational plans; establishing criteria and guidelines for assessing data quality; serving as a QA information focal point; auditing to ascertain effectiveness of QA implementation; and identifying and developing QA training programs.

The goals and policy of EPA's QA program is to ensure that all environmentally related measurements (data collection activities) regulated and supported by or for EPA produce data of known quality. The quality of data is known when all components associated with its derivation are thoroughly documented, such documentation being verifiable and defensible. Verifiable is defined as the ability to prove or substantiate any claim or result related to the documented record. Defensible is defined as the ability to withstand any reasonable challenge related to veracity or truthfulness.

In order to establish quality assurance solidly in all data collection activities U.S. EPA issued Order 5360.1. This order establishes policy and program requirements for the conduct of quality assurance (QA) for all environmentally related measurements performed by or for the Agency.

To ensure that all environmentally related measurements (data collection activities) meets U.S. EPA Quality Assurance Policy and requirements, the following organizations should develop and implement a Quality Assurance Project and/or laboratory plan:

* EPA Regional Program Offices (primarily special projects)
* EPA's contractors
* State Agencies
  State contractors
* NPDES & POTW Permittees
* RCRA Permittees
* Laboratories preforming analytical services (directly or indirectly) for support of programs regulated by U.S. EPA
* Other organizations under formalized agreements.

Some laboratories may integrate their QA Plan into specific QA Project Plans (ie. State Laboratories, Permittee's laboratories, and Superfund contractors). However, our office recommends that all laboratories prepare and maintain a laboratory QA plan.

II. Where and how can QA Project Plan be integrated.

Listed below are several options that can be employed by preparers.

Option A: A separate identifiable QA Project Plan.

* Option B: The QA Project Plan can be integrated with Work Plans.

* Option C: The QA Project Plan can be integrated with Waste Analysis Plans (RCRA Permittees).

* Option D: The QA Project Plan can be integrated with Permits POTW, NPDES and RCRA Permittees).

What ever option is choosen the QA Project Plan must meet the minimal requirements as set forth in this guidance document.

* Whenever this option is chosen a "QA Projected Plan locator page" must be inserted in the table of contents of the document.

IIa. For laboratories:

A separate identifiable Laboratory QA Plan should be prepared and maintained at the facility.

III. Document Control

Purpose: Document control will serve to provide

- an easy, convenient way of preparing the QA Project, laboratory plans, and standard operating procedures.
- A easy way to revise and update the elements of QA plans and standard operating procedures.
- a focal point for internal/external audits and inspections.
- reviewers and inspectors a means by which deficiencies and corrective actions can easily be referenced in reports.

Minimum Requirements:

All Quality Assurance Project, Laboratory plans and standard operating procedures must be prepared using a document control format consisting of following information placed in the upper right-hand corner of each document page:

- Section Number _____
- Revision Number _____
- Date (of revision) _____
- Page _____ of _____

IV. Standard Operating Procedures (SOPs)

Purpose: Generally, simply citing a published method is not adequate. Published methods rarely have all of procedural details, and those that do generally have to be modified for the application or facilities at hand. The development of SOPs are fundamental for review and laboratory audit/inspection processses.

Developing SOPs:

Standard Operating Procedures (SOPs) shall be detailed documents describing who does what, when, where, how and why, in a stepwise manner. These SOPs shall be consistent with National SOPs endorsed or issued by Program or Regional Offices. They shall be sufficiently complete and detailed to ensure:

1. Data of known quality and intergrity are collected to meet the monitoring objectives.

2. The minimum loss of data due to out-of-control conditions.

SOPs shall be:

1. Adequate to establish traceability of standards, instrumentation, samples, and environmental data.

2. Simple, so a user with basic education, experience and/or training can properly use them.

3. Complete enough so the user/reader follows the directions in a stepwise manner through the sampling, analysis, and data handling process.

4. Consistent with sound scientific/engineering principles.

5. Consistent with current EPA regulations and guidelines.

6. Consistent with the manufacturer's specific instrumentation manuals.

SOPs shall provide for documentation sufficiently complete to:

1. Record the performance of all tasks and their results.

2. Explain the cause for missing data.

3. Demonstrate the validation of data each time they are recorded, calculated, or transcribed.

SOPS should be addressed in all QA Project or Laboratory Plan as outlined below:

° Standard Operating Procedures (SOPs) must be prepared for all routinely used sampling, analytical and management methods or protocols.

° SOPs must meet the minimum criteria as identified in "Developing SOPs" (See previous section).

° In cases where published methods have all the procedural details, with little or no modifications, photocoping the appropriate procedures will normally be adequate. However, it must meet the minimum criteria as identified in "Developing SOPs".

° In either case (development of specific SOPs or photocoping of published methods), the SOPs must be

- documented (using document control format)
- reviewed annually
- contain a cover page indicating who reviewed the SOP and the data of review.

° To accomplish these objectives, SOPs should address the following types of items:

1. General network design.
2. Specific sampling-site selection.
3. Sampling and analytical methodology.
4. Probes, collection devices, storage containers, and sample additives such as preservatives.
5. Special precautions, such as holding times and protection from heat, light, reactivity, and combustibility.
6. Federal reference, equivalent, and alternate test procedures.
7. Instrumentation selection and use.
8. Calibration and standardization.
9. Preventive and remedial maintenance.
10. Replicate sampling and analysis.

11. Blind and spiked samples.
12. Quality control procedures such as inter- and intra- field or laboratory activities.
13. Documentation procedures.
14. Sample custody and handling procedures.
15. Sample transportation procedures.
16. Safety.
17. Data handing/evaluation procedures.
18. Precision, accuracy, completeness, representativeness, and comparability procedures (control charts, calculations, statistical tests, etc.).
19. Service contracts.
20. Document control.
21. Corrective action procedures.

Element 1. Title Page (For both QA Project and Laboratory Plans)

Purpose: Primarily the title page provides a means of identifing the organization responsible for preparing the QA Plan and it will serve as documentary evidence that all appropriate responsible individuals have reviewed and approved the QA Plan. It will also serve to document the date of approval and provide a means of tracking the review and approval process.

Minimum Requirements:

The following information must be included on the title page:

° The title/name of the Project, Facility, or Laboratory.

° The name of the organization that is responsible for the Quality Assurance of the Project, Facility, or Laboratory.

° If a contractor is preparing the QA Project Plan for an organization (see above), then the contractor also must be identified.

° At the bottom of the title page, provisions must be made for the signatures of approving personnel.

QA Project Plans:

a) For in-house projects
   1) Project Officer
   2) QA Officer (not from from the Office of Quality Assurance)
   3) Robert G. Forrest, Chief Office of Quality Assurance U.S. EPA Region VI.
   optional 4) Laboratory personnel (Directors, Section Chiefs, QA Lab Officials).

b) For State and EPA Contractors (i.e. CERCLA)
   1) The organization's Project Manager/Officer
   2) The organization's QA Official
   3) EPA's Project Officer
   4) Robert G. Forrest, Chief
      Office of Quality Assurance
      U.S. EPA Region VI
   optional 5) Laboratory personnel (Directors, Section Chiefs, QA Lab Officials).

c) For State Contractors

1) Contractor's Project Manager/Officer
2) Contractor's QA Official
3) State Agency's Project Manager/Officer
4) State Agency's Project QA Official
5) EPA's Project Officer
6) Robert G. Forrest, Chief
Office of Quality Assurance
U.S. EPA Region VI
Optional 7) Laboratory personnel (Lab Directors, Section Chiefs, etc.)

d) For Permittees

1) Permittee's Project Manager/Officer
2) Permittee's QA Offical
Optional 3) State/City Project Manager/Officer
Optional 4) State/City QA Offical
Optional 5) EPA Project Officer
Optional 6) Robert G. Forrest, Chief
Office of Quality Assurance
U.S. EPA Region VI

Laboratory QA Plans:

a) For State Laboratories

1) Laboratory Director/Manager
2) Laboratory QA Offical
3) State Agency QA Offical
Optional 4) Laboratory Section Chiefs

b) For Commercial and Permittee Laboratories

1) Laboratory Directors/Managers
2) Laboratory QA Offical
3) Laboratory Section Chiefs
4) Permittee's Program Managers

Element 2. Table of Contents

The QA Project Plan Table of contents must address each of the following:

° A serial listing of each of the 16 QA project plan elements* (components).

° A listing of any appendices which are required to augment (to facilitate complete review) the QA Project Plan as presented (i.e., standard operating procedures, field manuals, work plans, operations plans, etc.)

° At the end of the Table of Contents, list the individuals on the title page and any other individuals (i.e., contracted lab) receiving official copies of the QA Project and any subsequent revisions.

- The individuals responsible for distributing the QA Project Plan and any subsequent revisions.

a) For EPA in-house projects
1.) EPA Project Officer

b) For State Agencies
1) The State Project Officer

c) For Contractors/Permittees
1) The Organization's Project Managers

d) For Laboratories
1) The Laboratory's Directors/Managers

° Serial listing of all 16 quality assurance project plan component is required, as listed below. Each component must be included and addressed for each project plan.

1) Title page with provision for approval signatures

2) Table of contents

3) Project description

4) Project organization and responsibility

5) Data quality objectives for measurement data in terms of precision, accuracy, completeness, representativeness and comparability

5a) Laboratory Data Quality Objectives*

6) Sampling procedures

6a) Good Laboratory Practices*

7) Sampling custody

8) Calibration procedures and frequency

9) Analytical procedures

10) Data reduction, validation and reporting

11) Internal quality control checks and frequency

12) Management, performance, technical systems, and data quality audits, and frequency

13) Preventive maintnance procedures and schedules

14) Specific routine procedures to be used to assess data precision, accuracy and completeness of specific measurement parameters involved

15) Corrective action

16) Quality assurance reports to management

*For Laboratory's not intergrated in a formal QA Project Plan.

° The serial listing of each of the 16 QA project plan elements (components) are the same, except number 5 which should be entitled "Laboratory Data Quality Objectives" and number 6 which should be entitled "Good Laboratory Practices (GLP)".

° If a laboratory also performs field activities then number 6 Sample Procedures must be addressed and number 6a will be added, to address Good Laboratory Practices (GLP).

Element 3 Project Description

Purpose: To provide sufficient information (on a project) for integration into and evaluation of the remaning elements (components) of the QA Project Plan. It must be complete enough to evaluate the appropriateness of Data Quality Objectives, sampling design, sampling and analytical methods, etc.

For Projects

This Element should address the following items:

A. Background Information and Previous Data Assessments

- A comprehensive (chronological) discussion of the project/site history, environmental setting (physiography, geology, hydrogeology, etc.), summary resultrs of data previously collected (chemical, biological, and physical parameters; matrices, etc.) previous data assessments (statistical results), summary of previous QA reports, and any other QA related information (i.e. previous data quality objectives, previous project goals).

B. Project Objectives (Purpose) and Scope

- A comprehensive statement addressing the project's objective (purpose). This item can be addressed in Element 5, if so, please reference Element 5 in this section.

D. Revisions (continuous projects)

- This element should be revised annually to provide updated information and changes. This element will require the inclusion of Parts A & B (above) of the previous year.

C. Schedule of Tasks and Milestones

- Both activities and milestones need to be stated in specific and measureable terms, so their timely attainment or non-attainment can be easily observed and documented.

- This item should consist of a list of activities and milestones which will lead to the accomplishment of the project purpose (objectives).

For example:

- dates anticipated for start and completion of the project,
- initiation of sample collection,
- sample analysis, data review and reporting,
- data validation and data assessments,
- final QA report preparation, and
- other applicable activities.

E. Data Usage. (can be addressed in Element 5)

This section should consist of a statement outlining the intended data usage so that appropriate review and evaluation can be made on the Data Quality Objectives, sampling and analytical methods, and any other QA/QC components of the QA Project Plan. When applicable, secondary uses of the data should also be identified.

For Laboratories

The following items should be addressed:

A. A comprehensive discussion of the laboratory's overall objective/purpose of thiS QA Program. Our office recommends that specific Laboratory/company policies be devloped and documents.

Some examples are listed below:

° To maintain an effective, routine quality control program to measure and verify laboratory performance.

° To meet data quality requirements for accuracy, precision and completeness through the use of proven or recommended methodologies.

- To provide sufficient flexibility to meet specific data quality requirements.

- To identify and provide corrective actions as soon as possible to avoid any possible adverse affect on data quality.

- To monitor and assess the operational performance of the laboratory on a routine basis including internal and external audits.

- Maintain complete written records of documentation chain-of-custody, analytical SOPs, calibration and preventive maintance SOPs, data validation and reduction procedures, etc.

- Other items that laboratories should address include:

  - resources to maintain QA
  - document control
  - external review of QA program
  - etc.

PROJECT ORGANIZATION AND RESPONSIBILITY

Purpose: To provide documentory evidence of what inter- and intraorganizations are participating in the QA Project or Laboratory plan. It serves to identify the individuals within each organization who are responsible for Quality Assurance (both program personnel and QA Office/ Officer). It also provides as a means for tracking, auditing, assessing training needs, and for developing and improving QA planning.

There are two distinct lines of responsibilities: a) the program/laboratory/facility personnel and b) the QA officer. The decision makers and resource manager's responsibilities within programs offices, laboratories/facilities must be documented. Because of management responsibilities to making decisions and allocation of resources, they must be responsible for the quality of data, equipment/instruments, facilities and field/laboratory functions. QA Officer's responsibilities must also be identify and document in order to reduce biases and provide the necessary external quality control assessments of QA Plans.

Minimum Requirements:

- This element must clearly identify and document all inter- and intra-organizations (i.e. contractors, labs) that are participating in each project.
- For each organization that is identified, individuals must be identified (including all laboratory sample custodians) by name and his/her responsibilities must be documented.
  - Must include the Project or Laboratory QA Officer's responsibilities.
  - Must include program/management personnel responsiblities.
- The QA project plan should contain a flow chart identfying the organizations and line of authority.

Below are some previous program personnel and QA officers responsibilities that should be developed and documented in each QA Plan (Project and Laboratory). These include, but not limited to:

Program/Project Manager Responsibilities

- Ensure Subcontractor Procurement meet QA/QC requirements
- Assignment of duties of the Project (lab.) Staff and orientation of the staff to the QA needs and requirements of the project (lab).
- Ensure all approved project-specific (lab-specific) procedures and internally prepared plans, drawings and reports meet QA drequirements.
- Serve as liasion (with QA official) between the Project Staff and other internal or external orgnanizations or organizational sub-units.
- Serve as the "collection point." for Project Staff reporting of noncomformances and changes in QA project documents and activities.
- Other

Field Coordinator Responsibilities (Lab. Dept. or Section Heads)

- Will be responsible for all field activities including those of subcontractors.
- Ensure that all field equipment/instrument meet performance criteria and calibration requirements
- Ensure proper labeling, handling, storage, and shipping requirements have been meet.
- Ensure all appropriate chain-of-custody procedures have been followed.
- Assist the QA Official in implementing any field audits.
- Will coordinate with line management and QA Official the procurement and control of equipment/instruments to ensure they meet QA or QC requirements of the project (or Laboratory).
- Other

Laboratory Director/Manager Responsibilities

- General supervision of laboratories
- Collaboration with the Project Manager (Permittee) in establishing quality sampling and testing programs.
- Schedule and execution of testing program.
- Serve as liasion between the Laboratory Staffs and other groups
- Serves as the "collectin point" for Laboratory Staff reporting of nonconformances and changes in laboratory activities
- Notification of the Laboratory and Quality Assurance Groups of specific laboratory nonconformances and changes
- Maintenance of laboratory data and checkprints while the project, or testing phase, is in progress
- Relese of testing data and results
- Calibration of equipment
- Storage of samples.

QA Officer Responsibilities:

a. Be the official organizational contact for all QA matters for the project. For example QA project plan implementation, sampling and analytical methodologies, Data Quality Objectives (DQOs), field and laboratory audits, management and data quality audits, PE and QC studies, etc.

b. Actively identify and respond to QA needs, resolve problems, and answer requests for guidance or assistance. For example field sampling problems (limited supplies of sample container's), transportation problems (holding time conflicts), etc.

c. Review, evaluate and approve QA project plans prior to our office (EPA Region 6 Office of Quality Assurance) review, evaluation and approval/non-approval.

d. Provide guidance in the development of QA project plans to each respective organizations program offices, management offices and project/program managers or officers.

e. Ensure that management, data quality, field and laboratory audits are performed on QA Project Plans.

f. Actively track the progress of all QA tasks in Project Plans (from preplanning to data assessments) and consult periodically with program/project managers.

g. Prepare and submit all QA reports (with recommendations and comments) to the appropriate line managers in their organization and to EPA officials.

h. Assure that appropriate corrective actions are taken on all QA tasks when, where and however needed.

i. Ensure that data of known quality and integrity are avialable for each planning (DQOs) and report phase (valid data).

Note: Although some of the these responsibilities may be delegatyed out, the ultimate responsibility still lies with the Project QA Official

* * The Project QA Official must be identified and documented in each QAPjP before full approval can be granted.

Element 5. Data Quality Assurance (QA Objectives)

This element is the most important section in any QA project plan. DQOs and all background information are fundamental to the development of a sound sampling design approach and of the remaining QA project plan elements.

Our office (Office of Quality Assurance) does not set DQOs, but only evaluates the appropriateness of DQOs to the sampling plan and the other elements within the QA project plan.

Purpose of DQO's

All data are subject to some error. Different types of error may be introduced at different stages of data collection. Some types of error can be controlled, while others cannot be controlled but can be recognized and described. Some types of error can be quantified while other can only be described qualitatively. The overall purpose of preparing detailed plans for data collection and quality assurance is first, to make sure that an appropriate level of control is exercised over sources of error that can be controlled (i.e., sampling variability) and second, to make sure that sufficient information is obtained to describe all known sources of error to the extent possible (i.e., old/new well design or construction).

The quality of a data set is represented in terms of five characteristics of the data: precision, accuracy, representativeness completeness, and comparability (referred to as PARCC). Brief explanations of these characteristics follow.

Precision - refers to the level of agreement among repeated measurements of the same characteristic.

Accuracy - refers to the difference between an estimate based on the data and the true value of the parameter being estimated.

Completeness - refers to the amount of data that is successfully collected with respect to that amount intended in the design.

Representativeness - refers to the degree to which the data collected accurately reflect the population, group or medium being sampled.

Comparability - refers to the similarity of data from different sources included in a single data set.

During the planning of a project or program that will involve the collection of envir onmental data, it is the responsibility of both the managers and technical personnel to define how they intend to use the data and to determine the quality of data needed to support that use.

With respect to all data collection activities the following pre-planning questions must be answered:

1) Is there a decision(s) to be made, a question(s), or some other type of problem to be solved?

2) Will the decision(s) or answer(s) depend in part on measurement data?

3) Will the data input to the decision(s) come from data based conclusions?

If the answer to the above questions are yes, then the decision(s) or question(s) should be clearly stated in order to establish the purpose for collecting data.

Also, each conclusion requiring environmental data should be clearly stated so that the specific data needed for that conclusion can be identified.

The next step in defining DQOs is to develop statements of the "universe" to which the conclusion should apply, of the level of uncertainty that will be acceptable for the conclusion, and of the amount of time and the level of resources that will be used to collect data needed for the conclusion.

The definition of the universe is needed to develop options for the sampling design. A sampling design, among other functions, defines how data collectors will identify and select the particular sites or "units" of the environment on which chemical, biological, or physical measurements will be made. Any universe may be subdivided (stratified) in different ways, and each of the subgroups may be studied to a greater or lesser degree. The choices made in in defining the sampling strata, selecting the sampling units, and allocating the number of measurements to be made for each stratum will affect the cost of collecting data and the ability to make valid conclusions about each of the strata as well as about the universe as a whole. The Program/Project Officer must have a clear definition of the universe of interest in order to design a program that will generate data that are properly representative of that universe.

The statement about the level of uncertainty associated with each conclusion will be used to determine what types and levels of error which may be tolerated in the data. No measurements system is free of error; thus, no conclusion based on measurement data can be absolutely certain. One of the central ideas behind the development of DQOs is that the level of uncertainty associated with a conclusion may be controlled through the proper design of data collection procedures and the associated QA and QC programs. By controlling the uncertainty associated with the conclusions, i.e. the components of a decision, the ultimate risk of making an incorrect decision can also be controlled.

In order to develop a design that achieves a balance between different sources of error and that controls each source of error to an appropriate level, the Program/Project Officer must investigate the anticipated effect of major sources or error on the precision and accuracy of each conclusion requiring data. These major sources include human error, error introduced by assumptions and approximations in statistical models, sampling error, and measurement error. The Program/Project Officers will need to determine how error introduced from each of these sources affects the conclusions and will need to calculate the expected precision and accuracy of each of each conclusion, taking all of the major sources of error into account. The calculations will involve assumptions about details of a sampling design being considered (e.g., total number of samples to be collected and their distribution among strata) and assumptions about the values expected in the variables to be measured. The method employed in calculating the expected precision and accuracy of each conclusion will depend on certain aspects of the data collection approach (i.e., what quantities will be measured directly and what quantities will be estimated) and on the nature of the quantity that will constitute each conclusion (e.g., mean, proprotion, percitile, slope, etc.).

The statements of time and resources will be used for making trade offs between the type and quality of data that are needed and the amount of time and money required to collect the data. Rough estimates of the time and resources limits must be known up front for the staff to develop reasonable alternatives for the decision-maker's consideration. In addition, the staff should consider as an option that the time (unconstrained) not be associated with obtaining quality information needed to make the decision.

If all of the issues just described are adequately addressed, the Program/ Project Officer's efforts will generate the following products:

- a clear understanding of each of the conclusions requiring measurement data.
- final statements of the acceptable levels of precision and accuracy associated with each of the conclusions dependent on measurement data.

° for each conclusion dependent on measurement data:

- a final definition of the population to which the conclusion is intended to apply.
- definitions of the variables to be measured.
- statements of the acceptable levels of precision and accuracy for the measurements to be made.
- a quantitative description of the effect of major sources of error (including more than measurement error) on the precision and accuracy associated with the conclusion).
- final estimates of the time and resources required to collect the data.

The final statements of the acceptable levels of precision and accuracy associated with each of the conclusiions responds to the precision and accuracy componenet of PARCC. The definition of the population associated with each conclusion addresses representativeness. The issues of "completeness" and "comparability" are included implicitly in dealing with precision, accuracy and representativeness. Missing data ("completeness") may comprise accuracy by introducing additional bias. Missing data may also comprise representativeness if there is an inordinate effect on certain of the sampling strata. On the issue of comparability, if a conclusion is expected to apply to a defined population, then the data must be comparable across that population and among any defined subpopulations (strata).

Because of the complexity of the relationship among the PARCC terms, our office's (Office of Quality Assurance) emphasis in reviewing DQOs will be to ensure that all of the necessary elements are included, and not that each of the PARCC terms be expliciyly and individually addressed.

Minimum Requirements:

° A statement of the decision (s) that depend (s) on the results of this data collection activity.

° If the data collection activitly is of an exploratory nature and not formally linked with a regulatory decision, then a clear explanation of the purpose for which environmental data are needed.

° Statements of each specific question that will be addressed in the data collection activity and the type of conclusion that is anticipated as an appropriate

answer to each question. The conclusions should depend only on measurements.

° A clear statement of the way in which each conclusion of the study will be represented, in terms of the results of staticical calculations made with the measurement data. For example:

- estimates of population parameters, such as a mean, proportion or percentile;
- estimated distributions of the variables accross the population sampled;
- estimates of dose, exposure, or environmental effects based on calculations with the data.

° Statements of the acceptable levels of precision and accuracy associated with each of the conclusions dependant on measurement data as follows:

- a statement of the acceptable amount of variance or imprecision (e.g., either confidence intervals or probabilities of incorrectly accepting or rejecting a hypothesis (Type I and Type II errors.)

- a description of any expected bias, including a statement of acceptable amount and direction of bias if this can be anticipated.

° A definition of the population to which each of the conclusions is intended to apply, including definitions of all subpopulations or strata.

° Definitions of the variables (e.g., ambient concentration of polluntant "a" in medium "b", measured in "x" units) that will be measured.

° The acceptable levels of precision and accuracy for the measurements to be made.

- for each matrix (medium) and parameter (variable), provide a table of the objectives for: a. Accuracy b. Precision c. Sentivity or method detection limits.

° A flow chart or spread sheet illustrating the relationship between the measurement data and each conclusion that will be made with the data. The chart should diagram the steps that will be needed in order to evaluate the data and draw a conclusion. The chart should also present the results of statistical analysis used to evaluate the effects of major sources of error on the precision and accuracy of each conclusion dependent on the data.

*For Laboratories.

Minimum Requirements

° For each matrix (medium) and parameter (variable) provide a table of the analytical data quality objectives for:

- Accuracy
- Precision
- Sentivity or method detection limit
- Completeness

° Other sources of error that should be dicussed, include, but are not limited, to the following:

- Laboratory Practices (See Element Number 6a)
- Outliers (they should be statistically determined)
- Reduction and validation errors.
- Internal quality control procedures.
- other

ELEMENT 6. SAMPLING PROCEDURES

Purpose: This element should succinctly describe the sampling rationale, sampling design, sampling procedures, and all other components of a project's collection activities. Inadequate planning will often lead to biased, meaningless, or unreliable results; good planning, on the other hand, can can produce valid results. The quality and utility of analytical data depends critically on the validity of the sample and the adequacy of the sampling design. The selection of the optimum sampling design is one of the most important factors influencing the reliablity of data. Please refer to Data Quality Objectives (ELEMENT 5).

Minimum Requirements for QA Plans

° Provide sufficient documentation of the sampling rationale (supported by the project desciption), sampling design, sampling procedures and other sample collection activities to enable reviewers to adequately evaluate the appropriateness of this element to the Data Quality Objectives, analytical procedures, internal quality control samples and procedures and other elements of the project or laboratory plan (if laboratory is envolved with sampling activities).

- a succinct justification of the project sampling rationale by matrix location, strata, population, measurement parameter or any other charateristics.

- a detail description of the sampling design

  a) specifing the locations of the sampling sites
  b) number of samples to be collected per matrix
  c) collection frequency
  d) the population to be sampled (including subpopulations)
  e) defining the sampling strata
  f) other relevant factors which may influence the design of the sampling approach; i.e., homogeneity of the universe, accessibility of the sampling area, sampling conditions, well design or construction, etc.

° Provide a map showing sampling sites, strata and other relevant factors (i.e., well locations, atypical habitats, etc.).

° Provide flow diagram(s) or charts(s) delineating sampling program operations.

° Identification of sample custodian(s). (need not indentify, if identified in ELEMENT 4).

° Provide a complete description of the sampling procedures or SOP(s). These procedures should be documented in the QAPjP as an appendix.

° Provide a table detailing sample preservation methods, maximum holding times and types of containers to be used.

° Document all special conditions for preparation of sampling equipment and containers to aviod sample contamination (i.e., containers for organics should be solvent-rinsed; containers for tracemetals should be acid-rinsed; containers for bacteria should be sterilized).

- must include specific decontamination procedure(s).

° Provide examples (exhibits) of forms, notebooks and documents to be used in recording data collection activities (See ELEMENT 7).

° Provide detailed descriptions and/or criteria of Good Field or Management Practices (also see ELEMENT 6a).

- The following Good Field and/or Management Practices should be developed (** written procedures or SOPs) and implemented in all QA project and Laboratory Plans (where applicable):

**For each written procedure, the following information should be included:

1) the responsible individual(s).

2) the review and evaluation process and frequency of review

3) the quality control criteria (where applicable)

4) the filing and/or storage procedures and codes for retrieving those files (login and logout procedures).

A. Administrative procedures:

- ° correspondences (letters and memorandums)
- ° QA/QC reports
- ° Data reporting and checks
  - errors
  - completeness
- ° procurement procedures (QC criteria)

B. Documentation:

- ° Field activities (sample tags, chain of custody forms, notebooks, etc.).
- ° Procedures for filing and storages of records
- ° Records retention time frames (Storage)

C. Review and evaluation:

- ° Sampling plans (site investigation plans, project operation plans, etc).
- ° Sampling designs (statistical or professional judgement).
- ° Field construction activites (well drilling, foundations, dikes, soil liners, leachate collection systems, etc.)
- ° Field Standard Operating Procedures (on a annual basis)
- ° Field instrument and equipment quality control criteria in procurement requests.

D. Quality control procedures:

- ° To ensure adequate supplies and spare parts (standards, reagents, preservation material, sample containers, etc.).
- ° Field decontamination procedures.
- ° Corrective actions on equipment/procedural problems or failures.
- ° Standard operating procedures are implemented.

- Maximum holding times and proper sample containers.
- Field quality control samples and their frequencies.
- Field or management data validation procedures.
- Storage, packaging and shipment of samples.
- Field calibration/preventative maintenance procedures.

E. Data processing, review and reporting:

- Quality control checks on procedures and frequencies
- Computer quality control checks on inputs, outputs, and verification of softwares
  - procedures
  - frequency of checks

ELEMENT 6a: GOOD LABORATORY PRACTICES

Purpose: Laboratories inherently have activities prior to and following analysis which directly or indirectly affect the quality of data. To ensure that reliable and defensible data has been generated and that all sources of error (internally and externally) have been identified (See ELEMENT 5), every laboratory must maintain an acceptable level of Good Laboratory Practices (GLPS).

Minimum Requirements:

- Provide a general description of GLPs that have been developed and implemented in your laboratory.
- Provide a table detailing the sample preservation technique, maximum holding times and the types of containers required per parameter (variable) or parameter group.
- Document all special conditions for preparation of sampling equipment and containers to avoid sample contamination per parameter group (i.e., organics, trace metals, bacteria, radiochemical parameters).
  - Include all specific routinely used decontamination procedures.
- Provide complete Standard Operating Procedures for recording data in forms, notebooks, computers, etc. and how records are to be identified and stored. (also see ELEMENT 6).
- Provide a flow chart outlining the major laboratory activities.
- Provide detailed description's and criteria for Good Laboratory practices not addressed in other elements. See the following pages.

The following Good Laboratory and Management Practices should be developed and implemented in all QA Projects and Laboratory Plans (were applicable):

A. Administrative Procedures:

1. Records filing and storage procedures
2. Correspondance procedures (letters, memorandums, etc.)
3. QA/QC reporting procedures
4. Data reporting procedures
   - Quality control checks on errors and completeness.
5. Procurement request (quality control criteria).

B. Facility Quality Control Requirements:

1. Should include, but not limited to, the following items:

   a. ventilation
   b. compressed air
   c. humidity
   d. temperature
   e. electricity and voltage controls
   f. noise levels
   g. storage (cold room, chemicals, walkin incubators, etc.)
   h. location of microbial, chemical, radiochecical laboratory sections (i.e., the microbial and chemical lab sections must not be located in the same room/area without a physical division/partion.

2. Quality control criteria should be established for each item identified.

3. Quality control criteria should be incorporated into procurement requests.

4. Should identify the responsible individual that will ensure the quality of the items identified.

C. Equipment/Instrument Quality Control Requirements:

1. Items that should be covered include, but not limited to the following:

   a) analytical instruments/laboratory equipment.
   b) furnaces
   c) incubators
   d) generators
   e) refrigerators
   f) laboratory hoods

g) equipment/instrument parts
h) equipment/instrument services contracts
i) chemical, microbial, radiochemical and volumetric tolerance of laboratory storage containers.

2. Quality control criteria should be established for each item identified.

3. Quality control criteria should be incorporated into procurement request.

4. Should identify the responsible individual that will ensure the quality of the items identified.

D. Laboratory Material Quality Control Requirements:

1. Should include, but not limited to, the following items (for each analytical method):

a) grades of reagents
b) grades of solvents
c) grades of gases
d) grades of membrane filters
e) grades of microbial media
f) grade of distilled/deionized water

2. Quality control criteria should be established for each item identified (per analytical method).

3. Quality control criteria should be incorporated into procurement request.

4. Should identify the responsible individual that will ensure the quality of the items identified.

E. Storage Requirements for Laboratory Material:

1. Items that should be covered include, but not limited to, the following:

a) reagents, solvents, gases
b) microbial media
c) samples, standards, blanks
d) sample extracts
e) radiological materials, and samples
f) light sensitive reagents and solvents.
g) microbial cultures
h) Hazardous waste, extracts, etc.

2. Quality control criteria should be established for each item identified.

3. Quality control criteria should be incorporated into storage procurement requests (also see C.)

4. Should identify the responsible individual that will ensure the quality of the items identified.

F. Disposal of Hazardous Waste:

1. Should develop and implement disposal procedures

2. Identify and establish quality control criteria for the disposal of hazardous waste.

3. Quality control criteria should be incorporated into equipment, supplies, containers, and other procurement requests.

4. Should identify the responsible individual that will ensure proper storage of hazardous waste.

G. Data processing, review and reporting:

1. Items that should be covered include, but not limited to, the following.

a) manual data processing procedures
b) computer data processing procedures
c) data package completeness

- raw data
- calculations
- calibration graphs, charts
- strip charts
- GC/MS printouts
- method detection limit
- etc.

d) manual data package review
e) computer data inputs and outputs reviews
f) verification procedures for computer software
g) quality control checks (procedures) and frequencies for a thru f above.

- manually
- use of reference materials (for computerized instruments)
- use of more rigorous software programs.
- etc.

2. Quality control criteria should be established for data processing, reviews, and reporting.

3. Quality control criteria should be incorporated into equipment and supplies (i.e., computers, softwares, paper printing quality, etc.).

4. Should identify the responsible individual that will ensure the quality of the data processing, reviews, and reporting.

H. Glassware Cleaning Requirements

1. Items that should be covered include, but not limited to, the following:

   a) cleaning based on substances to be removed
   b) cleaning based on analytical requirements
   c) cleaning based on sampling requirements
   e) cleaning based on biological requirements

2. Quality control criteria should be established for each item identified (down to specific methods, if required).

3. Quality control criteria should be incorporated into cleaning material procurement requests.

4. Should identify the responsible individual that will ensure the quality of the items identified.

I. This section should reference the other elements in the QA plan were Good Laboratory Practices are addressed.

For example: ELEMENT 7: Sample custody
ELEMENT 8: Calibration procedures
ELEMENT 9: Analytical procedures
ELEMENT 10: Data reduction, validation and reporting
Etc.

ELEMENT 7. SAMPLE CUSTODY PROCEDURES

Purpose: Sample custody procedures are necessary to maintain and document sample possession; to adequately establish and/or support the use of sample data in potential enforcement, regulatory or legislative actions.

Our office recommends that EPA National Enforcement Investigation Center (NEIC) or equivalent sample identification, documentation and chain-of-custody procedures be used.

(NEIC Policies and Procedures, EPA-330/9-78-001-R, Revised February 1984).

The following Sample Custody should be adopted.

A sample is under custody if:

1. It is in your possession, or
2. It is in your view, after being in your possession, or
3. It was in your possession and you locked it up, or
4. It is in a designated secure area.

Minimum Requirements

Field

- Document the procedures for preservation of reagents or supplies which become an integral part of the sample.
- Document the procedures for identifying samples to be collected.
  - Prepared sample labels
- Document the procedures and forms (notebooks) for recording the exact location, analysis to be performed, sample history, sampling conditions, etc.
- Document the field custody procedures and provide examples of all forms that will be used during the project.

Laboratory

- Document the procedures for receipt of samples.
- Document the forms (notebooks) for recording (logging) samples received/transfered within the laboratory.
- Document the laboratory custody procedures and provide examples of all forms that will be used during the project.

Project Documentation

It is the responsibility of all organizations to ensure that all project documents issued to or generated by organizations will be accounted for when the project is completed. Therefore:

- Develop and implement procedures for documenting projects (Refer to NEIC Policies and Procedures, EPA-330/9-78-00-R, Revised Feb., 1984.)
  - serialized document control system.
  - document inventory procedures
  - an evidentiary filing system

Sample Identification:

The method of identification of a sample depends on the type of measurement or analyses performed. When in-situ measurements are made, the data are recorded directly in logbooks or field data records, with identifying information (project code, station numbers, station location, date, time, samplers), field observations, and remarks. Examples of in-situ measurements include pH, temperature, conductivity, flow measurement, continous air monitoring, stack gas analysis and OVA.

Samples, other than in-situ measurements, are identified by a sample tag or other appropriate identification (hereafter referred to as a sample tag).

These samples are removed and transported from the sample location to a laboratory or other location for analysis. Before removal, however, a sample is often separated into portions depending upon the analyses to be performed. Each portion is preserved in accordance with applicable procedures and the sample container is identified by a sample tag. The information recorded on the sample tag should include the following:

Project Code

Station Number

Date

Time

Station Location

Samplers

Remarks

Preservative used

Type of analysis required

Lab Sample No. (May be completed by the receiving laboratory)

The sample tag contains an appropriate place for designating the sample as a grab or a compositeand identifying the type of sample collected for analyses. When used for air samples, the sampler may use the remarks section to designate the sequence number and identify the sample type. The Project Officer will detail procedures for completing tags used for soil, sediment, and biotic or other samples. The sample tags are attached to each sample or container.

After collection, separation, identification, and preservation, the sample is maintained under chian-of-custody procedures discussed below. if the composite or grab sample is to be split, it is aliquoted into similar sample containers. Identical information is completed on the tag attached to each split and one is marked "Split". In a similar fashion, tags will be marked for "Blank" or "Duplicate" samples.

Field logbooks are used to document all field activities and will ensure the validity of the samples collected. All information of the field activities should be recorded into a logbook. The logbook(s) should include the following information:

- Location of the sampling points
- Purpose of the sampling (i.e., defining pit areas, plumes, etc.)
- The environmental setting
- The number and amount of samples taken or required
- Weather conditions
- Field observations and measurements
- Description of sampling points
  - photographs
  - maps
- Date and time of collection(s)
- Type of preservative used
- Analysis, laboratory distribution or storage requirements
- The types and quantities of standards and/or reagents used

Field Custody Procedures

1. Collect only the number of samples neeeded to represent the media being sampled. To the extent possible, determine the quantity and types of samples and sample locations prior to the actual field work. As few people as possible should handle samples.

2. The field sampler is personally responsible for the care and custody of the samples collected until they are properly transferred or dispatched.

3. Sample tags shall be completed for each sample, using waterproof ink unless prohibited by weather conditions. For example, a logbook notation would explain that a pencil was used to fill out the sample tag because a ball point pen would not function in freezing weather.

4. The Project Officer should determine whether proper custody procedures were followed during the field work and decides if additional samples are required.

Transfer of Custody and Shipment

1. Samples are accompained by a Chain-of-Custody Record. When transferring the possession of samples, the individuals relinguishing and receiving will sign, date, and note the time on the record. This Record documents sample custody transfer from the sampler, often through another person, to the analyst in a mobile laboratory or at the laboratory.

2. Samples will be packaged properly for shipment and dispatched to the appropriate laboratory for analysis, with a separate custody record accompanying each shipment (e.g., one for each field laboratory, one for samples shipped, driven, or otherwise transported to Lab). Shipping containers will be padlocked or sealed for shipment to the laboratory. The method of shipment, courier name(s) and other pertinent information is entered in the "Remarks" section on the custody record.

3. Whatever samples are split with a source or government agency, a separate Receipt for Samples form is prepared for those samples and marked to indicate with whom the samples are being split. The person relinguishing the samples to the facility or agency should request the signature of a representative. If a representative is unavailable or refuses to sign, this is noted in the "Received by" space. When appropriate, as in the case where the representative is unavailable, the custody record should contain a statement that the samples were delivered to the designated location at the designated time.

4. All shipments will be accompained by the Chain-of-Custody Record identifying its contents. The original record will accompany the shipment, and the copy should be retained by the Project Officer.

5. If sent by mail, the package will be registered with return receipt requested. Freight bills, post office receipts, and Bills of Lading will be retained as part of the permanent documentation.

Receipt for Samples Form

A completed Receipt for Samples form complies with these requirements and is used whenever splits are provided. This form must be completed and a copy given to the owner, opertor, or agent-in-charge even if the offer for split samples is declined. The original is retained for the Project Officer.

Laboratory Custody Procedures

1. A designated sample custodian accepts custody of the shipped samples and verifies that the information on the sample tags matches that on the Chain-of-Custody Records. Pertinent information as to shipment, pickup, courier, etc. is entered in the "Remarks" section. The custodian then enters the sample tag data into a bound logbook which should be arranged by project code and station number.

The laboratory custodian will use the sample tag number or assign a unique laboratory number to each sample tag and assure that all samples are transferred to the proper analyst or stored in the appropriate secure area.

2. The custodian distributes samples to the appropriate analysts. Laboratory personnel are responsible for the care and custody of samples from the time they are received until the sample is exhausted or returned to the custodian.

3. When sample analyses and necessary quality assurance checks have been completed in the field, the unused portion of the sample must be disposed of properly. All identifying tags, data sheets, and laboratory records shall be retained as part of the permanent documentation. Samples received by the laboratory should be retained until after analyses and quality assurance checks are completed. When investigative documents are requested, for the evidentiary file, all identifying tags are removed for retention in the permanent documentation. Sample containers and remaining sample material should be disposed of appropriately.

4. Samples of materials which have been associated with high hazard levels should received in a specialized regulated laboratory. This laboratory reduces the hazardous characteristics of these samples and prepares them for routine analysis. To avoid potential contamination, tags from samples received by the laboratory are not considered permanent documents and will not be incorporated into the evidentiary file. The laboratory will verify that the information on arriving sample tags is accurately recorded on the appropriate Chain-of-Custody Records and notify the project manager or officer of any discrepancies. The sample tag number is entered on the Chain-of-Custody Record in the "comments" column. regulated laboratory personnel will initial the entry after verifying sample tag data or resolving a descrepancy.

5. The laboratory will submit a memorandum to program officer when the project documents are assembled. The memorandum, to be retained in the evidentiary file, certifies that the sample tags have been appropriately disposed of together with the sample containers and any remaining portions.

6. Data magnetic tapes will be copied into the appropriate lab minicomputer disc files. The original tapes will then be stored in the locked cabinets and the disc data will be used for computer data processing.

ELEMENT 8. CALIBRATION PROCEDURES AND FREQUENCY

Purpose: Calibration procedures (analytical & field) and their frequencies (recalibration) serves as a quality control check on the bias of instruments during the portion of the analysis.

Minimum Requirements:

For each measurement parameter (or parameter group) the following information sholud be documented:

- Provide a written description, Standard Operating Procedure, or reference the applicable manufacture procedures (manual).
- Provide the frequency for recalibration (internally and externally).
- List the calibration standards to be used and their sources, including traceability procedures.
- Prepare a QA/QC review audit flow chart showing the organizational level and key individuals who will review the calibration procedures.
- The calibration procedures should contain, but not limited to, the following items:
  - equipment indentification number (code)
  - calibration schedule (in-house, externally)
  - any specific equipment specification that may be required
  - criteria for selecting equipment to meet any equipment specifications
  - specific step-by-step procedures
  - equipment calibration log sheet
    a) Date of calibration.
    b) All information pertain to calibration procedures (i.e., maintenance problems, equipment failures, etc.).

c) Document the individual who calibrated the instrument and

d) ensure that all adjustments have been made

e) Document all equipment failures.

f) Corrective action procedures (if instrument is out of order).

g) All information pertain to calibration procedures should be included (i.e., reocurring maintenance problems).

ELEMENT 9. ANALYTICAL PROCEDURES

For each matrix (or matrix group) and parameter the following information is required.

a) Provide a written description (SOP) of the analytical procedure or reference the applicable EPA, ASTM, or Standard Methods procedures.

b) Each analytical procedures should contain the sensitivity or method detection limit.

- This can be addressed in ELEMENT 5.

*Analytical procedures also includes geotechnicals, microbial, aquatic, biochemical, earth science methods or any other environmental measurement methods.

OFFICIALLY APPROVED OR RECOMMMENDED EPA PROCEDURES WILL BE USED WHEN AVAILABLE.

ELEMENT 10. DATA REDUCTION, VALIDATION AND REPORTING

Minimum Requirements:

For each major measurement parameter (or measurement method), describe the following items:

° Document the principal criteria that will be used to validate data integrity, at minimum it should include the following:

- Data Logging
  a) Verify all paperwork, chair-of-custody forms, etc.
  b) Verify all holding times, preservations and containers.
- Completeness of analytical data.
- Corrections of analytical data.
  a) a check on all mathematical calculations
  b) a check on all data transpositions.
  c) a check on all units of measure.
  d) a check on all significant figures.
  e) a check on all instrument's calibrations, tunings, and performances.
  f) etc.
- Accuracy
- Precision
- Representativeness

° Methods used to identify and treat outliners, all outliners should be statistically evaluated.

° Provide all equations used to calulate the concentration or value of the meassured parameters and reporting units or reference the applicable SOP or EPA, ASTM, Standard Methods procedures [If an SOP is referenced, (other than EPA, ASTM or Standard Method) then the SOP must be appendixed.]

° Provide a data flow chart from collection of raw data through storage of validated concentrations with the organization level and key individuals who will review or handle the data.

° Provide the reporting and the QA/QC review procedures (internally and externally).

ELEMENT 11. INTERNAL QUALITY CONTROL CHECKS.

Purpose: Internal and external Quality Control Check samples and procedures are used to provide a measure of the consistency of samples and to provide an estimate of variance and the bias in the collection process, handling processes (such as sample shipping, storage, and preparation), and analyses.

Other quality control checks that should be documented or referenced such as, construction and review of quality control charts (Shewhart or Cusum chart); calibration procedures; preventive maintenance procedures; data reduction/validation procedures; quality control check sample programs; performance evaluation studies; the traceability of instrument standards, samples and data; analytical and QC methods, sample preservation and transportation procedures; and audits.

Minimum Requirements:

- Identify and briefly describe each quality control check sample and procedures that is or will be incorporated into the project and that will meet the Data Quality Objectives of the project or Laboratory.
- For each quality control check sample and procedure document the frequency of use or review. Our office recommends that QC samples be analyzed at a 10% frequency.
- Provide a flow chart showing intergration of the quality control check samples, procedures and review procedures.

The table 11-1 presents the breakdown of QC samples used in previous projects (studies).

Table 11-1. Quality Control Check samples

Sample	Comments
Field Blanks	Analyzed to detect accidental or incidental contaminations.
Sample Bank Blanks (Method Blanks)	A field blank passed through the sample preparation and operators, after cleaning, to check for residual contamination.
Contamination Blanks	A field blank passed through equipment and/or samples to check for residual contamination.
Reagent Blank	A blank to check reagent contamination level.
Calibration Check Standard	A standard for extract matrix effects on recovery of known added analyte.
Spiked Sample (Field Matrix Spike)	To check for sample and extract matrix effects on recovery of known added analyte.
Total recoverable	A split sample (a second aliqueot) is digested by a more vigorous method to check the efficiency of the protocol method.

Sample	Comments
Split-Extract (Lab split)	To check sample, injection and instrument reproducibility.
Duplicate Sample	To determine total random error.
Triplicate Sample	The prepared sample is split into three portions to provide blind duplicates for the analytical laboratory and a third replicate for a referee laboratory to determine interlab precision.
Internal Standards (Spikes)	An analyte which mimics the behavior of target analytes and is added to extract prior to analysis, to check on instrument performance.
Surrogate Sample	An analyte which mimics the behavior of target analytes, and is added to field sample or lab extract, to check for sample/extract or extract matrix effects on recovery of known added analyte.
Indicator Sample	Usually a qualitative or semi-qualitative parameter (method) used to indicate the presents of specific analytes.

ELEMENT 12. MANAGEMENT, DATA QUALITY, TECHNICAL SYSTEM AND PERFORMANCE AUDITS

Purpose: Project audits provide assurance that the quality control job is being done effectively. Audits will serve to:

- Provide to management an on-going assessment of the quality of the results produced by the organizations data collection activities and how well data quality objectives (DQOs) are being met.
- Identify areas where improvement in the QA will result in increased reliability of data.
- Ensure that the QA program as defined by the QA Project Plan is implemented.
- Demonstrate that a organization is actively assessing the effectiveness of its QA program.
- Evaluate appropriateness of resource levels applied to QA.
- Provide a measure of the organization's commitment to effective corrective action when audits identify areas of concern.
- Provide suggestions for alternative ways of accomplishing QA tasks or dealing with QA problems.

Below are the four basic audits that each project (or laboratory) plan should describe (both in-house and extramurally). Some of these audits may be an ongoing process (Management), crossing over several projects, but affects each project and thus should be documented in each QA project plan.

Management Audits

Management audit is a systematic investigation to determine whether management functions and responsibilities related to environmental measurements are performed in accordance with appropriate quality assurance guidance. They are a review of the implementation of the approved QA plans. They evaluate the QA program of an organization responsible for environmental data collection activity in all its dimensions:

- The level of financial resources and personnel devoted to implementing the QA program.
- The level of management support.
- Tracking systems.

- Criteria for classifying data collection projects, according to how stringent the QA need to be and how extensive the documentation needs to be.

- Procedures for developing DQOs.

- Procedures for developing and approving QA Project Plans (QAPjPs).

- The Quality of existing QAPjPs.

- Procedures for developing and approving Standard Operating Procedures (SOPs).

- Procedures and schedules for conducting audits.

Data Quality Audits

Data quality audit is a systematic investigation to determine whether data derived from an environmentally realted measurement is of known quality. A data quality audit focuses on collected data and it will determine whether or not sufficient information exists with the data set to support an assessment of data quality. Data quality audits evaluates:

- A data set, or all the data sets of a particular project, against its data quality objectives (DQOs).

- Whether or not the organization collecting or using the data, performed its own date quality assessment, and

- Heeded the results of its assessment in terms of whether or not the dat could be used to support its decesion.

- Whether or not an organization identified deficiences (if they existed) and corrected the causes(s), both technical and managerial.

Technical Systems Audits (Field and Laboratory Audits)

Technical systems audit is a systematic investigation to determine whether data collection and analytical technologies are sufficient to meet the data quality objectives. Technical system audits evaluates:

- Field and analytical measurement procedures (SOPs).

- Field and laboratory chain of custody procedures and records.

- Internal quality control procedures.

- Control charts.

- Field and laboratory calibration procedures and records.
- Maintenance procedures and repair records.
- Field and laboratory corrective action procedures.
- Validation, reduction and reporting procedures.
- Equipment and facilities (field and laboratory).
- Support systems (field & laboratory).
- General laboratory cleanliness.
- Other

Performance Evaluation Audit

Performance evaluation is the means of evaluating the performance of laboratory technician and the instruction or analytical systems on which they work. A PE audit is accomplished by providing PE samples containing specific pollutants (in the appropriate matrix) unknown to the technician in their identity and/or concentration. Performance evaluations are implemented externally by the EPA Office of Quality Assurance, EPA Project Officers or laboratory management and enternally by the organization's QA Offical or Project Officer. Some National Program Offices, notably the National Pollution Discharge Elimination System (NPDES) and the Office of Drinking Water programs have annual nation-wide PE audits.

Minimum Requirements:

° Develop written procedures (SOPs) for audits. If audits have not been developed, a schedule for developing audits must be included.

° Describe how the audits will be intergrated and implemented [internally (routinely) and externally].

° Identify and describe all audits planned for the project or laboratory Include any current or recent EPA audits (i.e., PE Studies, laboratory audits within the last year).

° Document any in-house audits that may affect or be intergrated with specific project audits.

- Field and laboratory calibration procedures and records.
- Maintenance procedures and repair records.
- Field and laboratory corrective action procedures.
- Validation, reduction and reporting procedures.
- Equipment and facilities (field and laboratory).
- Support systems (field & laboratory).
- General laboratory cleanliness.
- Other

Performance Evaluation Audit

Performance evaluation is the means of evaluating the performance of laboratory technician and the instruction or analytical systems on which they work. A PE audit is accomplished by providing PE samples containing specific pollutants (in the appropriate matrix) unknown to the technician in their identity and/or concentration. Performance evaluations are implemented externally by the EPA Office of Quality Assurance, EPA Project Officers or laboratory management and enternally by the organization's QA Offical or Project Officer. Some National Program Offices, notably the National Pollution Discharge Elimination System (NPDES) and the Office of Drinking Water programs have annual nation-wide PE audits.

Minimum Requirements:

- Develop written procedures (SOPs) for audits. If audits have not been developed, a schedule for developing audits must be included.
- Describe how the audits will be intergrated and implemented [internally (routinely) and externally].
- Identify and describe all audits planned for the project or laboratory Include any current or recent EPA audits (i.e., PE Studies, laboratory audits within the last year).
- Document any in-house audits that may affect or be intergrated with specific project audits.

ELEMENT 13. PREVENTIVE MANITENANCE PROCEDURES.

Purpose: To insure that all facilities equipment (including field equipment) service's instruments and any other ancillary items that are available, are properly functioning and maintained.

Minimum Requirements:

° A description of how the responsible organization(s) monitors and controls facilities equipment, services instruments and any other ancillary items (Management SOPs).

° Describe what preventive maintenance will be covered, for example laboratory instruments, field instruments, water distillation or deionization unit, glassware washing machines, incubators, etc.

° What is the frequency for inspecting equipment, instruments and any other ancillary items (in-house and by certified inspectors).

° For each piece of equipment and instrument that has the potential to significantly altering data results (i.e., D.O. probe) or has the potential for significantly altering the allocation of resources (i.e., drilling apparatus) include a list of critical space parts that should be on hand to minimize downtime.

° Preventive maintenance procedures should contain, but not limited to, the following items (per instrument/equipment):

- specific step-by-step procedures.
- maintenance log sheets and/or schedules (in-house and externally by certified inspectors).
- due dates (if applicable) for maintenance.
- document the individual(s) responsible for ensuring maintenance has been made.
- document all maintenance performed, including dates of maintenances.
- document the corrective action procedures for preventive maintenance procedures which have not been followed, and the annual review procedures of the preventive maintenance procedures.

ELEMENT 14. SPECIFIC ROUTINE PROCEDURES USED TO ASSESS DATA QUALITY OBJECTIVES

Purpose: Data assessments are systematic procedures used for reviewing data set(s) against a set(s) of established criteria (Data Quality Objectives) to assure that the data meets the project goals. Please refer back to ELEMENT 5: Data Quality Objectives.

Minimum Requirements:

- Develop and implement data assessment procedures (program and laboratory office procedures).
- Provide a flow chart showing each phase of the data assessment review, including the mechanism for review of the data assessment procedures (network), the organizational level and the key individuals who will assess data and/or review procedures.
- Document all statistics to be used in the calculation of:
  1. Precision
  2. Accuracy
  3. Completeness
  4. Method detection limit
- Document the statistical procedures that will be employed to assess Data Quality Objectives (including confidence levels):

  Examples:
  1. Linear regression
  2. Analysis of Variance (ANOVA)
  3. Test of significances
  4. t-test for outliers
  5. Nonparametric tests
  6. etc.

ELEMENT 15. CORRECTIVE ACTION PROCEDURES

Purpose: To provide written requirements establishing and maintaining QA reporting or feedback channels to the approriate management authority to ensure that early and effective corrective action(s) can be taken when data falls below required limits. Each QA project plan shall describe the mechanism(s) to be used when corrective actions are necessary.

Corrective action should relate to the overall QA management scheme; who is responsible for taking corrective actions; when are corrective actions to be taken; who ensures that corrective actions are taken to produce the desired results, and what steps will be taken should corrective action not take place.

Minimum Requirements:

° Each measurement system must have predetermined limits to identify when corrective action is required, before data becomes unacceptable. Should include, but not limited to, the following items:

- Field equipment/procedural problems or failures.
- Laboratory equipment/procedural problems or failures.
- Control chart nonconformances.
- Broken or Lost Samples.
- Holding Times problems or failures.
- Calibration and Standardization problems and failures.
- Preventive and remedial maintenance problems.
- Sample custody and handling problems or failures.
- Sample transportation problems
- Documentation deficiencies or problems.
- etc.

- Identify the organizational level(s) and the key individual(s) responsible for initiating corrective action(s) and for approving corrective action(s).

- The Project QA Official must be notified of any major corrective action that results in a change in procedures or a loss of data. All nonconformances should be documented and reported internally (in-house) and in the final (annual) QA project report (See ELEMENT 16).

  - Therefore, the QA Project or Laboratory Plan should include procedures for documenting and reporting nonconformances.

ELEMENT 16. QA REPORTS

Purpose: The purpose of reports (communications) is to ensure that staff personnel (internally and externally) in the program offices can effectively develop and implement projects, perform activities, and resolve problems.

Minimum Requirements:

Internally

° Describe the internal mechanisms, SOPs, and reviews that are or will be performed on the measurement systems and data quality. These reports should include at a minimum:

- Periodic assessments of data quality objectives.
- Results of audits.
- Significant QA problems, corrective actions and recommended solutions.
- The level and individuals responsible for preparing the periodic reports (field, lab and management).

Externally

° Submit QA reports to the EPA Region VI Office of Quality Assurance (see below). The responsible individual for preparing this report should be the Project QA Official.

The Region VI Office of Quality Assurance will be tracking projects involving environmentally related measurements. One-time projects of 12 months duration or less, will require only a final QA report. Projects of longer duration, such as continuing multi-year programs, will require periodic QA reports to document implementation of the QA Project Plan. For example, continuous monitoring activities should be covered in an annual report summarizing the status of such projects for each annual budget period. The QA report on each project should be a separately identified Status Report containing:

A. QA management (any changes)

B. Status of completion of the QA project plan

C. Measures of data quality from the project

D. Significasnt quality problems, quality accomplishments, and status of corrective actions

E. Results of QA Performance audits

F. Results of QA Technical Systems audits

G. Results of QA Management and Data Quality audits

H. Assessment of data quality in terms of precision, accuracy, completeness, representativeness, and comparability

I. Quality Assurance related training

J. Assessment of indicators used in the project (when applicable)

C. Measures of data quality from the project

D. Significasnt quality problems, quality accomplishments, and status of corrective actions

E. Results of QA Performance audits

F. Results of QA Technical Systems audits

G. Results of QA Management and Data Quality audits

H. Assessment of data quality in terms of precision, accuracy, completeness, representativeness, and comparability

I. Quality Assurance related training

J. Assessment of indicators used in the project (when applicable)

ATTACHMENT 5

SAMPLE DOCUMENTATION FORMS

SAMPLE COLLECTION LOG

PROJECT NAME: Jacksonville Offsite
LOCATION: Jacksonville, Arkansas
PROJECT #

DATE:
TIME:

SAMPLE #
Sample Location Description

GC Purpose: PR = Predecon DE = Decon R1 = 1st Resample R2 = 2nd Resample FI = Final
VF = Verification EC = Equipment Check RM = Routine Monitoring
GC = General Characterization WI = Well Installation

Sample Type: AI = Air BU = Bulk CH = Chip CO = Core LI = Liquid OI = Oil (Liquid)
SE = Sediment SO = Soil WI = Wipe WA = Water

Composite? Y/N Comp. description

Sample Attitude: 01 = Horizontal 02 = Vertical 03 = Both

Elevation
Depth of Take
X-Axis
Y-Axis
Area or Volume Sampled

Sketch/Comments

	Floor/Area Code	Equipment Code	
Floor/Area	00 = Basement	01 = Wall	07 = Cabinet/Desk
Room	01 = First	02 = Ceiling	08 = Exterior Pipes, Beams, Duct
Zone	02 =	03 = Floor	09 = Door
Equipment	03 =	04 = Equipment	10 =
	04 =	05 = Vent System	11 =
	05 =	06 = Ambient Air	12 =

QA/QC CODE

QA/QC Code: QBL = Blank QRE = Rewipe QGS = Spike QDU = Duplicate QRI = Equipment Rinse QRIG = Original of QA/QC sample
QA/QC Partner

TM Lab: AU = Austin CE = Cerritos DI = Directors ED = Edison FM = FAS Mobile MK = Middlebrook PI = Pittsburgh SC = Santa Clara TM = TMS (Indianapolis)

03 Analysis Request: 01 = PCB 02 = PCDD/PCDF 03 = 2,3,7,8-TCDD 04 = other parameters

Analysis Status: 01 = Priority 02 = Analyze 03 = Hold

Film Roll No. Frame No.

Sample Team Prepared By
(Initials)

LST-30

FORM #084625-F8,REV 2 (10/87)

Attachment 5, Figure 1 Sample Collection Log

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